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# PHYSICAL REVIEW.

## ON THE FREEZING POINTS OF AQUEOUS SOLUTIONS OF NON-ELECTROLYTES.

By E. H. Loomis.

THE object of the work which is presented in this paper has been to test the validity of the van't Hoff constant for dilute aqueous solutions of non-electrolytes. Much work has already been done in this region, but it has been mostly confined to the investigation of cane sugar, ethyl alcohol and urea. The results in general have not been in accord with the van't Hoff theory. While the great confusion which the earlier results presented has largely disappeared with the more recent advances in the methods of measurement, still there remains much disagreement in the latest observations of the most careful observers, even in cases where the apparent exactness of the methods had lead the observers to regard their results as final.

Thus Abegg[1] finds for the molecular depression in the case of

| | |
|---|---|
| Cane Sugar, | 1.86 |
| Ethyl Alcohol, | 1.79 |
| Urea, | 1.87 |
| Dextrose, | 1.81 |

While Raoult's[2] latest values give for

| | |
|---|---|
| Cane Sugar, | 1.87 |
| Ethyl Alcohol, | 1.83 |

These results can not be looked upon as *constant*, since the esti-

[1] Zeit. Phys. Chem., XX., 1896, p. 207.
[2] Zeit. Phys. Chem., XXVII., 1898, p. 617.

mated experimental errors are of a much smaller order than would be required for such a conclusion.

## THE METHOD.

The apparatus is the same as that originally used by the writer, and described in the PHYSICAL REVIEW, Vol. I., 1893. The method is likewise unchanged in all essentials. It will be remembered that this method enabled the writer to overcome the most serious difficulty met with in attempts to measure the freezing points of solutions, namely, that of bringing the solution and its "ice" to their actual temperature of equilibrium. This difficulty is so troublesome and the experimental errors which arise in this connection are so great that I am not surprised that the complete solution of this difficulty after many months of the most tedious work left me entirely unarmed against another source of error much less difficult to overcome and of the most self-evident nature. This difficulty concerns itself with the manipulation of the *thermometer*. It was found necessary at the very outset to keep the thermometer at 0° C. when not in actual use. To effect this the thermometer was packed, *its whole length*, in ice in the ice cellar of the Strasburg Laboratory. Thus the *stem*, as well as bulb, was at 0° C. The temperature of the room in which the observations were made was on the average about 5° C., and it is thus obvious that the *stem* of the thermometer was gradually warming during the first series of observations each working day.

Hence these observations were lower than they would have been if the stem had come at once to the temperature of the room. These first observations were uniformly the ones which determined the zero point of the thermometer for the day, and thus all such zero points may be said to have been "too low." Since the stem range was 2°.5 C. and the thermometer was of the enclosed type with a thick glass wall, it is easy to believe that the error arising from this very obvious source could have reached as much as 0°.001 C. To avoid this it is, of course, only necessary to place the lower portion of the thermometer in ice and water and leave the "stem" at room temperature. This change was introduced at the beginning of the 1896 series. A second source of error arises also from the manipulation

of the thermometer. While it is of much less importance than the one already described, its discovery has led to a real simplification of the practice of the method, and so deserves attention. It relates also to the stem of the thermometer. That portion of the stem below the cork which supports the thermometer in the freezing vessel and above the surface of the solution must, of course, have a constant temperature if a series of independent observations on the freezing point of a given liquid are to agree. This was accomplished in the earlier work by keeping the freezing vessel with its contents for 20 minutes in a bath of ice and water before each observation of a freezing point. It was then transferred to a freezing mixture to induce freezing of the solution and then to the "protection bath" where the solution and its "ice" were allowed to come to equilibrium. While the great uniformity with which these changes were made would preclude the possibility of any very serious lack of constancy in the temperature of this intermediate portion of the stem, still there is a source of danger here. This becomes the more evident when it was discovered that, although the *length* of this unmarked portion of the stem is only that of 4 degrees on the thermometer, *actual measurement of the temperature range showed it to be 10 degrees.* This fact was unknown to me until after all the experimental work had been finished. It now seems probable that the small remaining experimental error of the present method will be eliminated when the difficulty is removed. Obviously it is necessary to have a thermometer made with the capillary reduced to the smallest possible size in this portion.

Without knowing at the time the real nature of the source of error I was always aware of its existence and overcame it by the long exposure of the whole apparatus to a temperature of 0° C. To still further overcome this difficulty and to facilitate the practice of the method the following change of procedure has been made. The freezing vessel, holding the thermometer and solution, is placed in a freezing mixture until an overcooling of 0°.3 C. is produced. It is then placed directly in the "protection bath," whose temperature is also 0°.3 C. below that of the freezing point to be observed. Here it is allowed to stand 15 minutes. It is then "touched off" with a tiny crystal of ice. The stirring and jarring are then begun and

continued for two minutes as usual. A reading of the thermometer is then made.

## THE ACCURACY OF THE METHOD.

It is plain that a method which claims to have any high degree of exactness must fulfil two experimental conditions:

1. In a series of observations on a given freezing point, the various observations must have a narrow range of variation. The present method originally showed a range of about 0°.0008 C. in a series of five entirely independent observations. By lowering the room temperature to about 0° C. this variation was reduced to the average value, 0.°0005 C., in the 1896 series, while the slight change in the practice of the method which allows the freezing vessel to stand in the "protection bath" instead of the ice and water bath for the fifteen minutes preceding the observation has reduced this to 0.°00046 C. in the present series. Many series of observations on the zero point of the thermometer gave the same result for each individual observation, while in some cases of the more concentrated solutions the variation has amounted to as much as 0.°0015 C. It is to be noticed that the variation, which now remains, may be wholly accounted for by a lack of uniformity in the temperature of the middle portion of the stem of only 0.°25 C. I am of the opinion that when this source of error is wholly suppressed, this very slight lack of constancy in a series of successive observations will be reduced still further.

2. The observed zero points determined from day to day on the thermometer must show only small variation. An examination of such a series of zero points throws much light upon the exactness of the method, since it is evident that any lack of absolute constancy in such a series must be accounted for either by assuming experimental errors, or irregular changes in the thermometer itself. When the variation is large the method is proportionally inexact. Unfortunately these zero points are generally not published. The latest work of Abegg is, however, an exception, and this example will serve to illustrate the importance of this criterion of a method's accuracy. He publishes a series of eight such zero points, presumably in the order in which they were made, though he fails to give

the dates.[1] I allow myself the privilege of submitting the series together with the barometer at the time.

| Zero Point. | Barometer. |
|---|---|
| 0°.7741 | 747 mm. |
| .7738 | 744.5 |
| .7736 | 741 |
| .7733 | 742 |
| .7724 | 741 |
| .7681 | 736.5 |
| .7670 | 732.5 |
| .7668 | 727.5 |

The total variation is 0.°0073 C. Reducing the readings to a common air pressure, say 740 mm. by use of a correction factor which the author himself experimentally determined (0°.0002 C. per 1 mm.). The series becomes

| | | | |
|---|---|---|---|
| 0.7727, | 0.7729, | 0.7734, | 0.7729, |
| 0.7722, | 0.7688, | 0.7685, | 0.7693. |

The range is thus reduced to about 0°.005. Thus of the original variation of some 0°.007 C. in *eight* observations, only 0.002 are accounted for in an experimental way, and yet he says of this series:

"Die Variationen der Einstellung rühren jedoch, wie eine nährere Betrachtung der Zahlen zeigt, sicher nicht allein von den Luftdruckänderungen her, sondern dürften auch kleinen zufälligen Verunreinigungen des destillirten Wassers zuzuschreiben sein, auf dessen genau gleiche Beschaffenheit kein besonderer Wert gelegt wurde." I have elsewhere remarked that it seems unwise to refer so great a variation in the observed zero point of the thermometer to accidental impurities of the distilled water used, since these impurities would need to be so great as to raise the water to the order of a $\frac{1}{1000}$ normal salt solution.

The series furthermore shows that the zero point of his thermometer was *falling*. During the six years that I have been observing the zero point on my thermometor, the zero point has been rising, whether it was in use or at rest. This is evident in every series except that of 1893, where the experimental errors were so great as to mask this rise of the zero point. I am persuaded that the greater part of

[1] Zeit. Phys. Chem., XX., 216.

these observed variations in the zero point of the thermometer are due to faulty methods.

The record of zero points for the series 1897, 1898 and 1899 is here submitted.

| Date. | Observed zero. | Barometer. | Room Temp. | Zero point corrected to 760 mm. and 0°C. | Depressions observed on the given zero. |
|---|---|---|---|---|---|
| 1897 | | | | | |
| Feb. 26 | 0.0510 | 761 | 2°C. | 0.0500 | Butyric Acid. |
| " 27 | 0.0517 | 769 | 2 | 0.0494 | Propyl Alcohol. |
| Mar. 7 | 0.0512 | 773 | 1 | 0.0486 | Cane Sugar. |
| " 16 | 0.0518 | 771 | 2.5 | 0.0490 | Ethyl Alcohol. |
| " 28 | 0.0505 | 759 | 3 | 0.0495 | Normal Butyl Alcohol. |
| Apr. 21 | 0.0521 | 773 | 3.5 | 0.0506 | Control for Sugar, M = 0.10. |
| 1898 | | | | | |
| Feb. 26 | 0.0520 | 760 | 3 | 0.0508 | Part of Methyl Alcohol. |
| Mar. 31 | 0.0542 | 760 | 5 | 0.0522 | Urea. |
| Dec. 29 | 0.0545 | 759 | 2.5 | 0.0537 | Part of Chloral Hydrate. |
| 1899 | | | | | |
| Jan. 2 | 0.0569 | 781 | 1 | 0.0530 | Chloral Hydrate and Acetone. |
| " 3 | 0.0558 | 773 | 1 | 0.0532 | Ether and Mannite. |
| " 7 | 0.0552 | 763 | 2 | 0.0540 | Urea. |
| " 10 | 0.0562 | 771 | 2 | 0.0536 | Control for Urea. |
| " 19 | 0.0566 | 766 | 4 | 0.0541 | Amyl Alcohol. |
| " 25 | 0.0555 | 750 | 3 | 0.0550 | Part of Amyl Alcohol. |
| " 28 | 0.0557 | 760 | 2 | 0.0549 | Aniline and $MgSO_4$.[2] |
| " 30 | 0.0556 | 759 | 2 | 0.0550 | $H_2SO_4$[2] and part of $MgSO_4$.[2] |
| " 31 | 0.0551 | 757 | 2 | 0.0548 | No depressions measured. |
| Feb. 1 | 0.0566 | 766 | 2 | 0.0548 | NaCl.[2] |
| " 11 | 0.0570 | 771 | 2 | 0.0544 | Acetamide.[2] |
| Mar. 18 | 0.0556 | 757 | 4 | 0.0545 | Control for Acetamide. |

These zero points are represented graphically in Fig. 1.

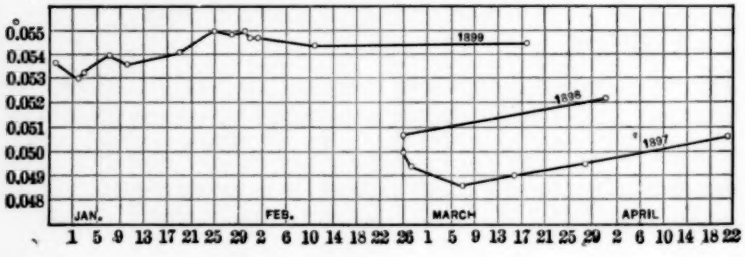



Fig. 1.

[1] Results reserved for a subsequent paper.

It needs to be stated that the zero point at the end of the 1896 series was 0.°045. Thus the slow rising of the zero point which has been observed before is still going on, though the rate is noticeably less. It is worth noticing that the variation in the zero point is such as to be largely accounted for by the well-known changes which a thermometer undergoes—a slow rise of the zero point. The exact uniformity in the rate of this elevation of the zero point for the greater portion of the 1897 period is certainly not other than accidental, but the very nearly uniform rise in the first part of the 1899 period and its almost exact constancy during the latter portion of the same period, are clearly indicative of the high degree of exactness which the method has attained.

The range of variation for the 1897 series is seen to be 0°.002 C. in six zero points, and in the 1899 series it is seen to be 0°.002 in thirteen zero points, extending through a period of three months.

In each case the greater part of this variation is accounted for by the obvious fact that the zero point has been rising. The remainder of the variation I think represents the experimental errors.

It is not without interest to observe that this thermometer has experienced a total rise of the zero point during the six years that it has been in use since it was corrected at the Reichsanstalt, amounting to not less than 0°.023 C. The rate has been about 0°.0003 C. per month. The rise during the period of use is noticeably more rapid than this.

Further, any attempt to judge the exactness of any method must take notice of the facts which Nerst and Abegg[1] so clearly set forth in connection with their study of the disturbances which the equilibrium temperature of a mixture of water and ice undergoes on account of the temperatures of the surrounding bodies and the heat developed by the stirring. In the statement of their results they have introduced a temperature called the convergence temperature, which may be defined as that temperature which the water *without the ice* would assume when it has come into thermal equilibrium with its surroundings. They showed that in case the conditions of the experiment were not so chosen that this convergence temperature was identical with the true temperature of equilibrium

[1] Zeit. Phys. Chem., XV., p. 681.

of ice and water, then the observed temperature of the mixture when it has come into thermal equilibrium with its surroundings is not the true temperature of equilibrium of the ice and water sought, and that in certain cases the measurement of depressions of freezing points would be affected by grave errors unless the observations were corrected in a manner shown by the authors.

They conclude that the observed freezing point of any liquid is never its true "freezing point" unless one of two conditions are met; either the convergence temperature must be coincident with the true freezing point, or the *rate* at which a liquid comes to temperature equilibrium when once it begins to freeze must be infinitely great. This may be accepted without hesitation. Then they express themselves in these words:

"Since the former condition has never yet been exactly fulfilled, it has been assumed in the earlier investigations that the equilibrium between the solid and liquid solvent takes place at an infinite velocity."[1]

I have elsewhere said that the "convergence temperature" played no rôle in the method which I have used.[2] From the very beginning of the work the disturbance which the temperature of a mixture of ice and water suffers on account of the temperature of its surroundings and the heat due to the stirring was well known to me, and the entire development of the method was always in the direction of eliminating these disturbances. Thus in the first brief notice of the work[3] I express myself on this point as follows:

"A fundamental difficulty lies in the fact that the temperature of a mixture of ice and water is influenced by the temperature of the surroundings, * * * * and a further difficulty consists in the fact that this influence, which is caused by the heat exchanges between the mixture and its surroundings, *and also by the heat developed by the stirring*, varies with the quantity and fineness of the ice present. In order thus that the temperature of a mixture of ice and water may be as nearly as possible the (true) freezing point (of the water), that is, the temperature at which the ice and water alone would be

[1] Zeit. Phys. Chem., XV., p. 683. 1894.
[2] Jour. Phys. Chem., I., p. 224.
[3] Ber. Berichte, 1893, XXVII., p. 798.

in equilibrium, it is necessary that these disturbing influences be eliminated." In the fuller publication of the work[1] stress is laid upon the success with which this was accomplished, aud data are then presented which enabled one to conclude that "the disturbing influences of the freezing bath and surrounding air have been so far eliminated that the *actual* freezing point of water, and so too of a solution, may be determined." This conclusion was drawn from a series of observations on the freezing point of water in which about one-half the individual observations were made with very large amounts of ice present, while the remainder were made with only traces of ice present. It was found that the average values of these two portions of the series were the same. But Abegg[2] reminds me that my conclusion that the convergence temperature was thus shown to be identical with the true freezing point under observation does not follow necessarily. Since, as he says, the same result would be found if the rate at which a mixture of ice and water comes to its equilibrium temperature is very great. The theory requires this rate to be infinitely great. Now simply put, this rate depends upon nothing save the rate at which the ice melts or the water freezes, and there is little need to talk about this rate being "very great" to say nothing about its approaching an infinite value. It is necessary to observe that my conclusion that the "convergence temperature" of my apparatus was coincident with the true freezing point of the solutions was the result of long experimental work which had no other aim than to bring about this essential result, and I have never had the slightes ground for doubting the soundness of my conclusion. It is for this reason that I have not thought it necessary to reopen this part of the investigation. But Abegg has kindly urged upon me the value of some direct test of the matter, and on March 7, 1899, I made the following experiment:

Room temperature 3°.5 C., barometer 742 mm. The observed freezing point of water was 0°.0520. To find the convergence temperature of the apparatus it is only necessary to proceed exactly as though a determination of the freezing point of the water were to be observed except that the water is not "touched off," so that the

[1] PHYS. REV., 1893, I., p. 213.
[2] Wied. Ann., 64, p. 490.

water comes to thermal equilibrium with no ice present. After a few minutes the thermometer showed 0°.056, and this was the final reading after ten minutes of stirring. Thus the convergence temperature of the apparatus when the air is at 3°.5 C. and the protection bath is 0°.3 C. is 0°.004 C. above the true freezing point of water. This difference between the convergence temperature of the apparatus and the freezing point of the water under observation is many times smaller than is necessary to insure the exactness of the method. The result of this experiment is exactly what I had every reason more than six years ago to believe was the fact: The convergence temperature plays no rôle in the results obtained by use of the present method. It should be added that sufficient uniformity in the stirring is had by keeping time to a "sing-song" the exact words of which have little scientific interest.

TABLE I.

| 1 Compound. | 2 $m$ | 3 Grams per liter of the solution. | 4 Sp. gr. of the solution in (3) $\frac{18°}{4°}$ | 5 Sp. gr. of the solution $m = 0.20$. | 6 Source of the material. | 7 Manner of Preparing Solution in (3). |
|---|---|---|---|---|---|---|
| Methyl Alcohol. | 1. | 32.02 | 0.9928 | 0.9975 | Prepared in Lab. | By direct weight, after drying. |
| Ethyl Alcohol. | 1. | 46.04 | 0.9901[1] | 0.997 | Squibb's 99.89%. | " " " |
| *n*-Propyl Alcohol. | 1. | 60.05 | 0.9894 | 0.9967 | Kahlbaum. | " " " " " |
| *n*-Butyl Alcohol. | 1. | 74 .06 | ..... | 0.997[7] | Kahlbaum. | " " " |
| Amyl Alcohol. | 0.1 | 8.81 | .... . | 0.997[2] | Kahlbaum. | " " " " " |
| Glycerine. | 1. | 92.04 | 1.0203 | 1.003 | Eimer & Amend. | Gerlach's Tables.[3] |
| Dextrose. | 0.9834 | 177.08 | 1.0664[4] | 1.0125[4] | Merck & Co. | Fresenius' Tables.[5] |
| Cane Sugar. | 1. | 342.1 | 1.1294 | 1.024 | Rock Candy. | By direct weight, after drying. |
| Mannite. | 0.5 | 91.04 | 1.0304 | 1.012 | Merck & Co. | " " " " " |
| Ether. | 0.5 | 37.03 | 0.9911 | 0.996 | Squibb's Abs. | " " " " " |
| Acetone. | 1. | 58.04 | 0.9908 | 0.997 | Kahlbaum. | Squibbs' Tables.[6] |
| Chloral Hydrate. | 1. | 165.4 | 1.0722 | 1.0159 | Kahlbaum. | Direct weight. |
| Aniline. | 0.2 | 18.61 | ..... | 0.9995 | Kahlbaum. | " " after drying. |

[1] Sp.gr., $\frac{20°}{4°}$.

[2] $m = 0.10$.

[3] Landolt and Börnstein Tabellen, 1895, p. 230.

[4] Sp. gr., $\frac{17.5°}{4°}$.

[5] Zeit. Anal. Chem., 1883, XXII., p. 454.

[6] Ephemeris, VII., p. 541.

[7] Assumed.

The present investigation includes the non-electrolytes, which are tabulated with the usual accompanying data in the opposite table.

### Methyl Alcohol, 1896.

The solution $m = 1$ was prepared from methyl alcohol which had been made by the saponification of methyl oxalate crystals with ammonia water in a manner which is described below. The tables of specific gravity furnished by Dittmar and Fawsitt[1] were used. But the specific gravity of the resultant normal solution was 0.99313 at 15°56C. and the solution according to these tables was thus 5 % too strong.[2] The observed depressions were accordingly corrected by this amount, reducing the observed molecular depressions to the almost constant value 1.73. This result was so surprising that it could not be accepted until all possibility of error in the concentration of the solutions was set aside. To this end nothing would avail except the attempt to prepare *pure methyl alcohol.* This I undertook to do. The work, however, was so great and was so slow of accomplishment that the publication of the large part of the experimental material of the years 1896, 1897 and 1898 had to be delayed to the present time. This will account for the confusion in the dates of the various series of observations. To prepare methyl alcohol the following method was used: The best methyl alcohol of commerce is converted into methyl oxalate by adding 800 cc. of the alcohol to a solution of 1000 gr. oxalic acid crystals in 400 cc. of sulphuric acid. When this is allowed to stand in a cool place the methyl oxalate separates out in an abundant crop of colorless crystals, which are drained and *washed with ice cold water.* The product has a marked "mouse nest" odor. The crystals are now digested with a strong solution of ammonia in water, using a glass flask provided with an "inverted condenser." This leads to the saponification of the methyl oxalate with the regeneration of methyl alcohol. It is then distilled and all of the distillate collected that will come over from a bath kept at 100° C. The product is about half water, the greater part of which is removed by the use of dry $K_2CO_3$ and

[1] Edinburgh Trans., XXXIII., p. 509.

[2] In the Princeton Bulletin, May, 1896, in publishing the value for a .1 normal methyl alcohol solution I used a correction factor of 3 per cent. by mistake.

CaO in the order named. The yield is scanty, and large quantities of the materials have to be employed, for the product must again be put through the oxalate process.

After this has been done the methyl oxalate has lost its odor. The resultant methyl alcohol is dried as before and then subjected to a long series of successive distillations from metallic sodium. The distillations were made backwards and forwards between two distillation flasks, each of which served in turn as distilling flask and condenser.

In this way no pouring of the alcohol from one vessel to another was necessary. Between each distillation the specific gravity of the alcohol was observed. Some twenty such distillations from small bits of sodium were made before the specific gravity had been reduced to a constant value. I think much of this work would have been unnecessary if I had learned earlier in the work that methyl alcohol when nearly *dry* takes water from the air, in spite of ordinarily careful stoppering, so rapidly that its specific gravity goes up three or four points in the fourth place of decimals during a single night. When this fact became known the exclusion of the moisture of the air received the utmost care, and the determinations of the specific gravity were made in a pyknometer so arranged that the alcohol could be transferred to it from the condensing flask without contact with the air's moisture. In this way the specific gravity was reduced to a constant value.

At 10° the specific gravity = 0.80065.

At 20° the specific gravity = 0.79133.

Water at 4°C. = 1.

The boiling point of this methyl alcohol

At 766.74 mm. is 64°.70C.

At 752.92 mm. is 64.23.

Thus at 760 mm. it is 64°.5C. (Gasthemometer, Reichsanstalt).

It needs to be observed that the boiling point was taken as usual with the entire stem exposed to the vapor and the bulb about 4 cm. above the liquid. A quantity of glass beads was put in the flask to insure uniform boiling. The entire product, except the last frothing traces, went over at the temperatures given above. I find that the slight rise of 0°.1—0°.2 which occurs at the last moment

is no indication of an impure product, but results wholly from the unavoidable "overheating" when any small quantities of the substance are in the flask. Thus I find that the *purest water* behaves in the same way.

While the specific gravity and boiling point of methyl alcohol have thus been very much lowered below the hitherto accepted values, I have no reason for thinking that a *dry* product has yet been obtained. Only the limit which the apparatus and drying method used in the present work have fixed has been reached. It is worth mentioning that I find that sodium continues to dry methyl alcohol long after dry copper sulphate and $P_2O_5$ have ceased to act. It is probable, then, that Carrara,[1] in his attempt to measure the dissociation of water in methyl alcohol did not succeed in getting a *dry* alcohol as the basis of his work.

The methyl alcohol prepared in the way described above *has lost all traces of its characteristic odor.* I am of the opinion that a slight odor still remains, though some who have examined the product do not admit this. The details of this purely incidental work will perhaps be given at some future time in case opportunity arises to measure some other important constants of pure methyl alcohol, some 40 grams of which I still have left.

From this alcohol a gram-molecular solution was made by direct weighing. Its specific gravity at 18° C. was found to be 0.99281 and at 15°.56 C. it was 0.99318. Thus my suspicion that the tables of Dittmar and Fawsitt are faulty in the region of great dilution is confirmed. Using this final normal solution I then prepared a tenth normal solution for the purpose of determining its freezing point as a control to the observations made in 1896. The result was exactly 1% higher than the value found in 1896, and I should accordingly correct the entire series by this amount. But unfortunately a confusion exists in the original notes which forces me to regard the specific gravity of the normal solution prepared in 1896, as probably wrong, so that I am unable to say as I should like to that the 1896 solution was 1% weaker than the final one used in the "control." I can do no more than to give the 1896 series and say that they may be 1% too small. At the first opportunity I shall repeat the entire series.

[1] Gazz. Chim. Ital., 1897, XXVII., p. 1.

*Methyl Alcohol, Feb.* 17, 1896.

| $m$ | $\Delta$ | $\frac{\Delta}{m}$ | $P$ | $m'$ | $\frac{\Delta}{m'}$ |
|---|---|---|---|---|---|
| 0.01 | 0°.0183 | 1.83 | 0.321 | 0.01 | 1.83 |
| 0.02 | 0.0362 | 1.81 | 0.641 | 0.02 | 1.81 |
| 0.03 | 0.0548 | 1.83 | 0.963 | 0.0301 | 1.82 |
| 0.05 | 0.0910 | 1.82 | 1.605 | 0.0502 | 1.81 |
| 0.10 | 0.1818 | 1.82 | 3.216 | 0.1005 | 1.81 |
| 0.20 | 0.3655 | 1.83 | 6.457 | 0.2018 | 1.81 |

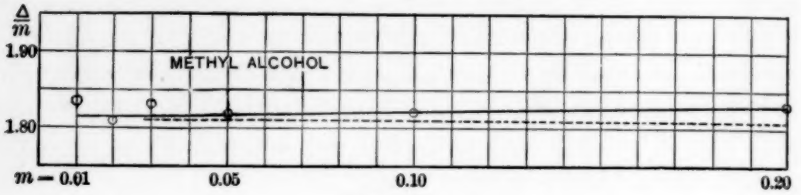



Fig. 2.

In the tables throughout this paper $m$ denotes the number of gram-molecules per liter of the solution; $\triangle$, the depression of the freezing point, and $\triangle/m$ is what is generally known as the *molecular depression.*

By the help of the specific gravity of the solution $m = 0.20$, it is easy to reduce the values of $m$ to the values $m'$ which denote the number of gram-molecules per 1000 grams of water in the solution. To this end the calculated number of grams of the substance per 1000 grams of water is given under $P$ in the tables. $m'$ equals of course the quotient of $P$ divided by the molecular weight.

The graphic representation of the results is presented with each table, using my usual method, in which the ordinates represent the the values of $\triangle/m$, and the abscissas the values of $m$. The dotted line gives the values of $\triangle/m'$.

The "curve" turns out to be a straight line. The observed values do not in any case differ from those that such a straight line would require by more than 0°.0003 C. The molecular depression is thus seen to be 1.82 in extreme dilution, increasing slowly to 1.83 in the region of greater concentration.

### ETHYL ALCOHOL, MARCH 16, 1897.

The solution, $m=1$, was made by direct weight from Squibb's "absolute alcohol." Dr. Squibb was kind enough to determine the

specific gravity of the product which he sent me directly before the can was sealed. He found specific gravity $\left(\frac{15°.6}{15°.6}\right)$, 0.79386. According to his table[1] the strength was 99.89%. The solution $m = 1$ had a sp. gr. $\left(\frac{20°}{4°}\right)$ 0.99005.

*Ethyl Alcohol, March* 16, 1897.

| $m$ | $\Delta$ | $\frac{\Delta}{m}$ | $P$ | $m'$ | $\frac{\Delta}{m'}$ |
|---|---|---|---|---|---|
| 0.01 | 0°.0181 | 1.81 | 0.460 | 0.01 | 1.81 |
| 0.02 | 0.0368 | 1.84 | 0.921 | 0.02 | 1.84 |
| 0.05 | 0.0920 | 1.84 | 2.312 | 0.0502 | 1.83 |
| 0.10 | 0.1849 | 1.85 | 4.633 | 0.1007 | 1.84 |
| 0.20 | 0.3707 | 1.85 | 9.314 | 0.2024 | 1.83 |

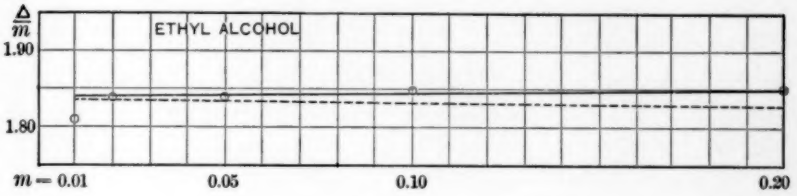



Fig. 3.

The comparison of these results with those of 1892[2] is instructive. For this purpose the earlier results are given below:

*Ethyl Alcohol, Dec.*, 1892.

| $m$ | $\Delta$ | $\frac{\Delta}{m}$ | Corrected Values. |
|---|---|---|---|
| 0.01 | 0°.0172 | 1.72 | 1.74 |
| 0.02 | 0.0351 | 1.76 | 1.78 |
| 0.04 | 0.0729 | 1.82 | 1.84 |
| 0.05 | 0.0894 | 1.79 | 1.81 |
| 0.10 | 0.1825 | 1.83 | 1.85 |
| 0.16 | 0.2927 | 1.83 | 1.85 |

Before making the comparison it must be remembered that the solutions of 1892 were known to be 1% too weak (see note, p. 282,

[1] Ephemeris, II., p. 541.
[2] PHYS. REV., I., p. 199.

l. c.). Applying this correction to the series we get the values shown in the last column of the table. The values at $m = 16$, $m = 0.10$ and $m = 0.04$ are identical with those in the new series. The values at $m = 0.01$, $m = 0.02$ and $m = 0.05$ fall below those of the new series. This comparison of the two series furnishes a very striking confirmation of the conclusion which has been reached in regard to the error which arose in the earlier work on account of packing the whole thermometer in ice when out of use. The zero point is therefore uniformly made too low and the curve of molecular depressions, which was found to be straight in the region of greater concentration, is made to curve considerably downward in the region of great dilution where the error in the zero point would be most felt. A second matter of interest appears in the very singular value for $m = 0.04$. In the paper of 1892, this observation is looked upon as incorrect only because it was so out of accord with the rest of the series, and I was forced to assume the possibility of an error amounting to $0°.0015$ C., an error which, apart from this single observation, I had no right to admit.

It now appears that this one observation was the only one that was right in the region of extreme dilution. The observations at that time required generally a whole day for the determination of the zero point of the thermometer and the freezing point of the solution, so that it is easy to believe that this single determination could have been so made as to escape the influence of the usual source of error.

As in the case of methyl alcohol the graphic representation of the results is best effected by a *straight line* which shows, allowing for errors in no case greater than $0°.0003$, that the molecular depression is *1.84 in extreme dilution*, and that it increases uniformly to 1.85 at $m = 0.20$.

It is a matter of very great importance as well as gratification that the last results of Raoult,[1] are so exactly in accord with these values that it is impossible to distinguish the two series when graphically represented on the scale of the present curves. Although my work was done some time before Raoult published his results, Raoult had no knowledge of it until after the publication of his work. The two series have been made by different observers.

[1] Zeit. Phys. Chem., XXVII.

in entire independence and *without the guiding hand of any theory* and must be looked upon as affording the most strikingly confirmation of each other.

### Propyl Alcohol, February 27, 1897.

The solution $m = 1$ was made by direct weight from Kahlbaum's product. The product was successively distilled from sodium as in case of methyl alcohol, though with much less care. The boiling point of the middle portion of a final distillate was constant within 0°.1 C.

The specific gravity of this portion, at 15° C., was 0.80798; at 20°C., 0.80406.

Its boiling point at 760 mm. is 97°.2 C. These values, as with methyl alcohol, are much lower than those hitherto accepted, due simply to the greater dryness of the present products.

*n-Propyl Alcohol, Feb.* 27, 1897.

| $m$ | $\Delta$ | $\frac{\Delta}{m}$ | $P$ | $m'$ | $\frac{\Delta}{m'}$ |
|---|---|---|---|---|---|
| 0.01 | 0.0189 | 1.89 | 0.601 | 0.01 | 1.89 |
| 0.02 | 0.0371 | 1.86 | 1.201 | 0.02 | 1.86 |
| 0.05 | 0.0936 | 1.87 | 3.015 | 0.0502 | 1.86 |
| 0.10 | 0.1858 | 1.86 | 6.015 | 0.1008 | 1.84 |
| 0.20 | 0.3723 | 1.86 | 12.191 | 0.2031 | 1.83 |

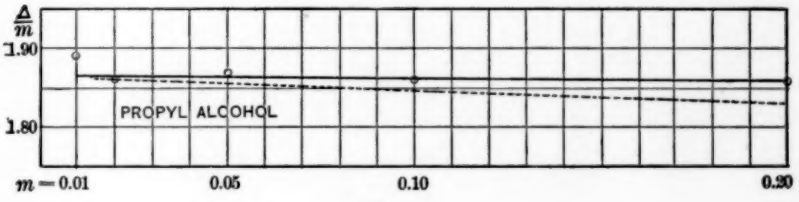



Fig. 4.

The graphic representation again is best effected by a straight line. The errors which must be assumed in drawing this conclusion do not exceed 0°.0003C.

The molecular depression is seen to be 1.87 in extreme dilution and to fall uniformly to 1.86 in the region of greatest concentration.

### N-BUTYL ALCOHOL, MARCH 28, 1897.

The solution $m = 1$ was made by direct weight from Kahlbaum's product. The quantity at my disposal was so small that no drying was possible. I assumed that there was 1 % water present and made allowance for this in making the weighings. Its specific gravity at 20° with a Mohr balance was $0.8095 \pm 0.0002$. An attempt to dry a sample obtained afterwards from the same source, with the hope that a "control" determination of the freezing point would enable one to "correct" the original series resulted in failure; since, in spite of the utmost care in the successive distillations from Na, the product did not show a constant boiling point within 5° C. I am unable to find that *n*-butyl alcohol has ever been prepared with such a degree of purity that the boiling point is any more constant than this, and I abandoned the idea of making any control determinations. I found the specific gravity of the product when dried with Na to be 0.8082 at 20° C. What degree of error there may be in the given values of the various concentrations I have no means of knowing. That the results are in accord with the rest of the alcohol series, of course, furnishes no ground for any conclusion in this matter.

*n-Butyl Alcohol, Mar.* 28, 1897.

| $m$ | $\Delta$ | $\frac{\Delta}{m}$ | $P$ | $m'$ | $\frac{\Delta}{m'}$ |
|---|---|---|---|---|---|
| 0.01 | 0.0189 | 1.89 | 0.741 | 0.01 | 1.89 |
| 0.02 | 0.0368 | 1.84 | 1.482 | 0.02 | 1.84 |
| 0.05 | 0.0926 | 1.85 | 3.72 | 0.0503 | 1.84 |
| 0.10 | 0.1863 | 1.86 | 7.47 | 0.1009 | 1.85 |
| 0.20 | 0.3723 | 1.86 | 15.08 | 0.2037 | 1.83 |

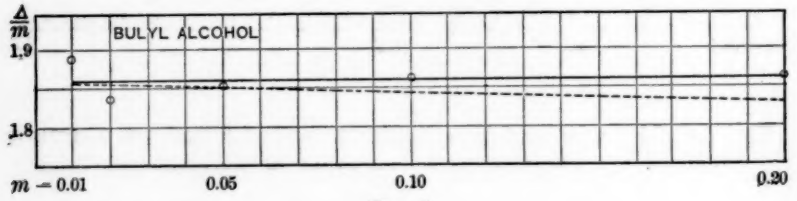



Fig. 5.

Again the graphic representation is a straight line. This conclusion requires the assumption of an error in no observation exceeding

0°.0003 C. The molecular depression in extreme dilution is 1.86 and this is the value also for all the concentrations.

### Amyl Alcohol, February 27, 1897.

The original product was Kahlbaum's "amyl alcohol" and is the ordinary amyl alcohol of fermentation. It was dried with Na. The final product had a boiling point constant within 1°.1 C. Its specific gravity was 0.8121 at 18° C. The solubility of amyl alcohol in water does not permit the solution $m = 0.20$.

*Amyl Alcohol, Feb.* 27, 1897.

| $m$ | $\Delta$ | $\frac{\Delta}{m}$ | $P$ | $m'$ | $\frac{\Delta}{m'}$ |
|---|---|---|---|---|---|
| 0.01 | 0°.0185 | 1.85 | 0.883 | 0.01 | 1.85 |
| 0.02 | 0.0372 | 1.86 | 1.766 | 0.02 | 1.86 |
| 0.05 | 0.0926 | 1.85 | 4.431 | 0.0503 | 1.84 |
| 0.10 | 0.1845 | 1.845 | 8.922 | 0.1013 | 1.82 |

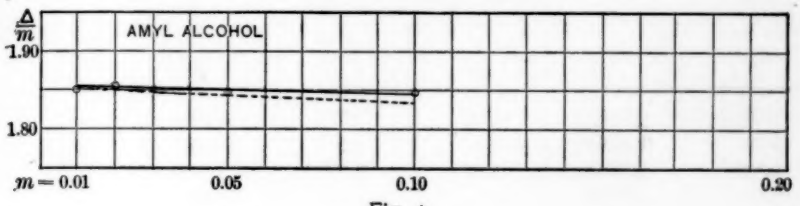



Fig. 6.

The graphic representation is again a straight line, with practically no error in any observation. The molecular depression in extreme dilution is 1.86 and this falls to 1.84 at $m = 0.10$.

### Glycerine, February 13, 1896.

The solution $m = 1$ was made by use of Gerlach's tables of specific gravity.

| $m$ | $\Delta$ | $\frac{\Delta}{m}$ | $P$ | $m'$ | $\frac{\Delta}{m'}$ |
|---|---|---|---|---|---|
| 0.01 | 0°.0186 | 1.86 | 0.922 | 0.01 | 1.86 |
| 0.02 | 0.0372 | 1.86 | 1.845 | 0.0201 | 1.85 |
| 0.05 | 0.0929 | 1.86 | 4.622 | 0.0502 | 1.85 |
| 0.10 | 0.1869 | 1.87 | 9.280 | 0.1008 | 1.85 |
| 0.20 | 0.3758 | 1.88 | 18.688 | 0.2031 | 1.85 |

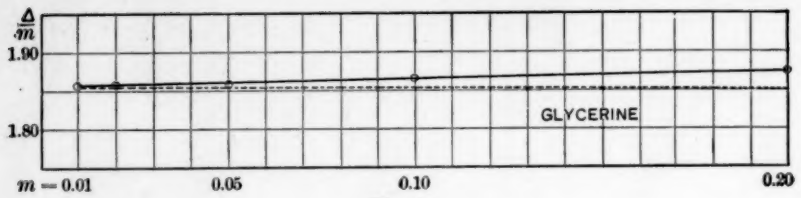



Fig. 7.

The graphic representation is a straight line, and this conclusion requires no appreciable errors to be admitted. The molecular depression is 1.86 in extreme dilution and rises to 1.88 at $m = 0.20$.

DEXTROSE, FEB. 22, 1896.

The product was from Merck and Co. It was not true to their label in regard to dryness, and so an approximate solution, $m = 1$, was made by weight and then corrected by use of the Fresenius tables.[1] The specific gravity of the approximate solution was 1.0664,

*Dextrose, Feb.* 22, 1896.

| $m$ | $\Delta$ | $\frac{\Delta}{m}$ | $P$ | $m'$ | $\frac{\Delta}{m'}$ |
|---|---|---|---|---|---|
| 0.0098 | 0.0185 | 1.88 | 1.774 | 0.0098 | 1.87 |
| 0.0197 | 0.0363 | 1.84 | 3.559 | 0.0198 | 1.84 |
| 0.0492 | 0.0916 | 1.86 | 8.927 | 0.0496 | 1.85 |
| 0.0983 | 0.1850 | 1.88 | 17.95 | 0.0997 | 1.86 |
| 0.197 | 0.3745 | 1.90 | 36.30 | 0.2016 | 1.86 |

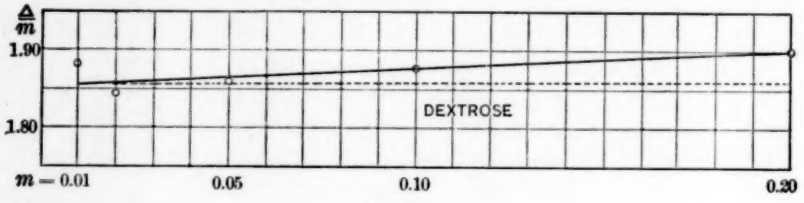



Fig. 8.

and was thus 1.66% too weak according to these tables. The concentrations in column ($m$) are corrected by this amount.

A true $m = 1$ solution, prepared from Kahlbaum's fine crystalline product, when freed from its bare trace of water by most careful drying, has been found to have a specific gravity at $\left(\frac{17.5}{17.5}\right)$, 1.0684

[1] Zeit. An. Chem., XXII., p. 454.

and at $\frac{18^\circ}{4^\circ}$, 1.0669. This is so nearly in accord with the Fresenius tables that I have accepted them with confidence.

The graphic representation is again a straight line, a conclusion which requires the admission of experimental errors reaching to 0°.0004 C.

The molecular depression is 1.85 in extreme dilution and rises to 1.90 at $m = 0.20$.

### Cane Sugar, March 7, 1897.

The solution $m = 1$ was made by direct weight from carefully selected crystals of "rock-candy." These were pulverized and dried over sulphuric acid. The solutions were made immediately before the observations on their freezing points.

*Cane Sugar, March* 7, 1897.

| $m$ | $\Delta$ | $\frac{\Delta}{m}$ | $P$ | $m'$ | $\frac{\Delta}{m'}$ |
|---|---|---|---|---|---|
| 0.01 | 0°.0187 | 1.87 | 3.432 | 0.01 | 1.87 |
| 0.02 | 0.0378 | 1.89 | 6.879 | 0.0201 | 1.88 |
| 0.05 | 0.0947 | 1.89 | 17.312 | 0.0506 | 1.87 |
| 0.10 | 0.1918 | 1.92 | 34.962 | 0.1022 | 1.88 |
| 0.20 | 0.3960 | 1.98 | 71.599 | 0.2093 | 1.89 |

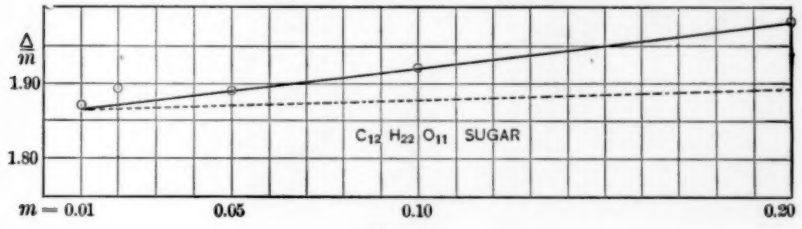



Fig. 9.

The graphic representation is again a straight line if an error of 0°.0004 be assumed at $m = 0.02$.

The molecular depression in extreme dilution is 1.86. It rises rapidly to 1.98 at $m = 0.20$.

These results should be compared with the series of 1892. It appears that, barring the downward curvature in the region of extreme dilution, which all the early series exhibited, the new re-

sults are exactly 1 per cent. higher than the old. The solutions however were not of the same strength, as appears from their specific gravity. Thus the solution $m = 1$, at 17°.5 C., has a specific gravity at 18°, 1.1294. The solution used in 1892 ($m = 1$ at 4° C.) had a specific gravity at 18°, 1.1285.[1] Accordingly, using the tables of specific gravity in the Kohlrausch Leitfaden, eighth edition, the old solutions were 0.6 per cent. too weak. The two series then are *parallel* and differ by 0.4 per cent., a difference probably less than the experimental errors of the method.

The latest values found by Raoult[2] are exactly parallel with these results when they are computed on like definition of a gram-molecular solution, but are exactly 1 per cent. higher. The agreement, while falling short of complete identity, as in the case of ethyl alcohol, is still not less striking, since the two series agree in that they confirm each other in the *fact of a uniform increase in the value of the molecular depression* with increase in the concentration. It is to be observed that the results of Raoult are expressible by a straight line without the smallest trace of an error, say at $m = 0.03$, when the error reaches 0°.0003 C. It is to be regretted that he did not examine solutions more dilute than $m = 0.03$, since his method clearly would justify this.

The two series are represented graphically in the annexed figure, in which $m$ is the number of gram-molecules per 1000 grams of water ($m'$ in the tables).

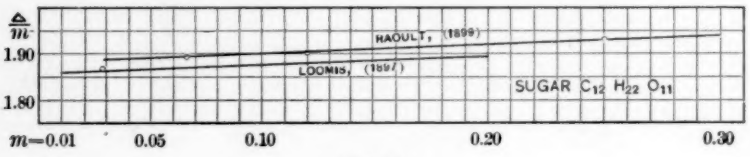



Fig. 10.

## Mannite, January 3, 1899.

The solution $m = 1$ was made by weight from Merck's product after drying at 100°C. to constant weight.

[1] The published value was 1.1286. This was reckoned without making allowance for air displacement, which is now done.

[2] Zeit. Phys. Chem., XXVII., p. 617.

*Mannite.*

| $m$ | $\Delta$ | $\frac{\Delta}{m}$ | $P$ | $m'$ | $\frac{\Delta}{m'}$ |
|---|---|---|---|---|---|
| 0.01 | 0°.0185 | 1.85 | 1.821 | 0.01 | 1.85 |
| 0.02 | 0.0371 | 1.86 | 3.656 | 0.0201 | 1.85 |
| 0.05 | 0.0931 | 1.86 | 9.169 | 0.0504 | 1.85 |
| 0.10 | 0.1874 | 1.87 | 18.44 | 0.1013 | 1.85 |
| 0.20 | 0.3807 | 1.90 | 37.33 | 0.2061 | 1.85 |
| 0.50 | 0.9835 | 1.97 | 96.92 | 0.5323 | 1.85 |

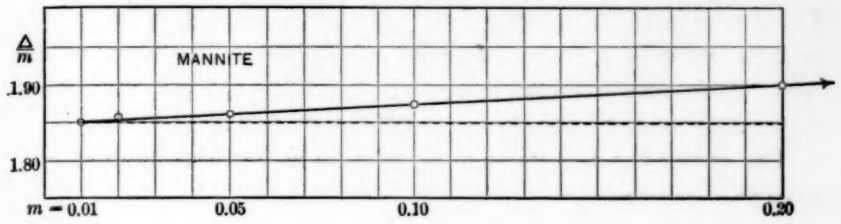



Fig. 11.

The results are again in a straight line if an error of 0°.0005C. be assumed in the observations at $m = 0.10$ and $m = 0.20$. The molecular depression is 1.86 in extreme dilution. It must be remarked that the results in the present case could be expressed by a curve slightly convex on the upper side and given a value for the molecular depression 1.84 in extreme dilution. I am of the opinion, however, that this is due to the distribution of the experimental errors in spite of the fact that an error of 0°.0005C. has to be admitted to make the results expressible by a straight line.

ACETONE, JANUARY 2, 1899.

The solution $m = 1$ was made from Kahlbaum's "Aceton aur der Bisulfitverbindung," by use of Squibb's tables of specific gravity.

*Acetone.*

| $m$ | $\Delta$ | $\frac{\Delta}{m}$ | $P$ | $m'$ | $\frac{\Delta}{m'}$ |
|---|---|---|---|---|---|
| 0.01 | 0°.0185 | 1.85 | 0.580 | 0.01 | 1.85 |
| 0.02 | 0.0372 | 1.86 | 1.163 | 0.02 | 1.86 |
| 0.05 | 0.0932 | 1.86 | 2.914 | 0.0502 | 1.86 |
| 0.10 | 0.1846 | 1.85 | 5.851 | 0.1008 | 1.83 |
| 0.20 | 0.3706 | 1.85 | 11.78 | 0.2030 | 1.83 |
| 1.00 | 1.914 | 1.91 | 62.22 | 1.072 | 1.79 |

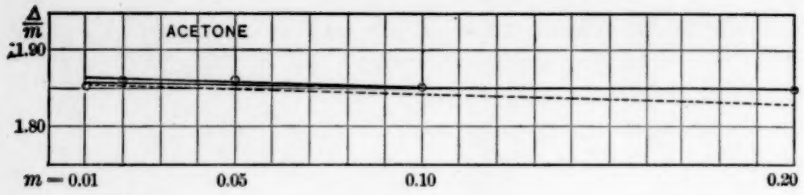



Fig. 12.

The representation of the *entire* series by a straight line is impossible. A curve, with its convex side downward, beginning at 1.86 in extreme dilution and running nearly straight in the region between $m = 0.01$ and $m = 0.20$ represents the results best. The errors necessary to this conclusion are inappreciable, while a straight line would require errors of 0°.001 at $m = 0.20$, and 0°.007 at $m = 0.05$.

The molecular depression is again 1.86 in extreme dilution and rises to 1.91 at $m = 1$.

### CHLORAL HYDRATE, JANUARY 2, 1899.

The solution $m = 1$ was made from Kahlbaum's product by direct weight, after exposure to sulphuric acid. The powdered crystals are volatile and it is impossible to bring the compound to a constant weight.

*Chloral Hydrate.*

| $m$ | $\Delta$ | $\frac{\Delta}{m}$ | $P$ | $m'$ | $\frac{\Delta}{m'}$ |
|---|---|---|---|---|---|
| 0.01 | 0°.0186 | 1.86 | 1.655 | 0.01 | 1.86 |
| 0.02 | 0.0373 | 1.87 | 3.318 | 0.0201 | 1.86 |
| 0.05 | 0.0924 | 1.85 | 8.315 | 0.0503 | 1.84 |
| 0.10 | 0.1875 | 1.87 | 16.696 | 0.1009 | 1.86 |
| 0.20 | 0.3760 | 1.88 | 33.66 | 0.2035 | 1.85 |
| 1.00 | 2.050 | 2.05 | 182.40 | 1.1028 | 1.86 |

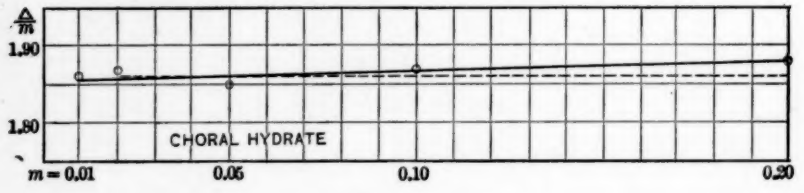



Fig. 13.

The graphic representation of the *entire series* shows that the results cannot be expressed by a straight line unless an error of more than 0°.001 be assumed at $m = 0.10$ and $m = 0.20$. As I have no right to assume so large an error, it must be said that here also a curved line with slight convexity on its lower side and practically straight in the region between $m = 0.01$ and $m = 0.20$, best represents the results. The necessary error for this conclusion is 0°.0005 C. in the observation $m = 0.05$.

The molecular depression is 1.86 in extreme dilution and rises to 2.05 at $m = 1$.

ANILINE, JANUARY 28, 1899.

Kahlbaum's product was distilled twice from sodium and made into a solution $m = 0.20$ by weight. The specific gravity of the aniline after the distillation was, at 15 C., 1.0260 and at 20° C., 1.0215.

*Aniline.*

| $m$ | $\Delta$ | $\frac{\Delta}{m}$ | $P$ | $m'$ | $\frac{\Delta}{m'}$ |
|---|---|---|---|---|---|
| 0.01 | 0°.0185 | 1.85 | 0.931 | 0.01 | 1.85 |
| 0.02 | 0.0372 | 1.86 | 1.867 | 0.0201 | 1.85 |
| 0.05 | 0.0914 | 1.83 | 4.681 | 0.0503 | 1.82 |
| 0.10 | 0.1811 | 1.81 | 9.407 | 0.1011 | 1.79 |
| 0.20 | 0.3549 | 1.77 | 18.97 | 0.2038 | 1.74 |

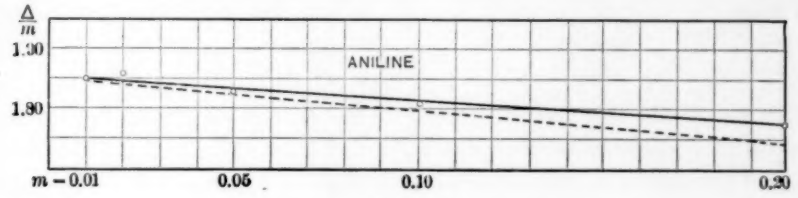



Fig. 14.

The results lie in a straight line, with an assumed error of 0°.0005 at $m = 0.10$.

The molecular depression is 1.86 in extreme dilution and falls rapidly to 1.77 at $m = 0.20$.

ETHER, JANUARY 3, 1899.

Squibb's "absolute ether" was distilled twice from sodium. It was then found to be no longer acted on by this drier. Its spe-

cific gravity at 15° C. was 0.7193, and its boiling point was 34°.3 C. at 760 mm. These values are much lower than the accepted values for these constants, save only the specific gravity, as found by Squibbs,[1] namely, 0.7189 at 15°.

*Ether.*

| $m$ | $\Delta$ | $\frac{\Delta}{m}$ | $P$ | $m'$ | $\frac{\Delta}{m'}$ |
|---|---|---|---|---|---|
| 0.01 | 0.0162 | 1.62 | 0.741 | 0.01 | 1.62 |
| 0.02 | 0.0336 | 1.68 | 1.486 | 0.0201 | 1.67 |
| 0.05 | 0.0856 | 1.71 | 3.724 | 0.0503 | 1.70 |
| 0.10 | 0.1734 | 1.73 | 7.486 | 0.1011 | 1.72 |
| 0.20 | 0.3468 | 1.73 | 15.10 | 0.2038 | 1.70 |

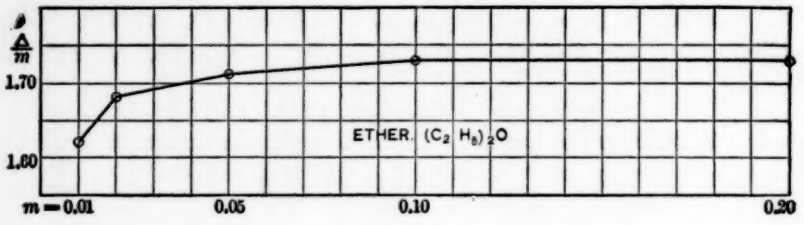



Fig. 15.

The graphic representation is a curve line with a pronounced convex side on the upper side. The molecular depression in extreme dilution can be obtained only by a very uncertain extrapolation which gives, say, the value 1.50. The molecular depression becomes constant at $m = 0.10$, with the value 1.73.

## General Discussion.

It is well known how van't Hoff has shown that the freezing point of a solution of any non-electrolyte in any solvent is theoretically capable of calculation by the formula,

$$\Delta = \frac{0.002T^2}{\lambda} \cdot \frac{G}{M}.$$

Where $\Delta$ denotes the difference between the known freezing point of the pure solvent and that of the given solution. $T$ is this known freezing point of the solvent on the absolute scale, while $\lambda$ is its heat equivalent of fusion. $G$ denotes the number of grams of the solute

[1] Ephemeris, II., p. 678.

per liter of the solution, and $M$ is its molecular weight. It is convenient to call $G/M$ the number of gram-molecules per liter, and to denote it by $m$.

Thus in the case of aqueous solutions, using the value accepted by van't Hoff as the most probable for $\lambda$, we have, for the lowering of the freezing point due to any non-electrolyte:

$$\Delta = \frac{0.002(273)^2}{79} \cdot m,$$

and accordingly the value of the molecular depression is

$$\frac{\Delta}{m} = \frac{0.002(273)^2}{79} = 1.89.$$

This is the *van't Hoff constant.*

The early work of Raoult covered a large range of organic substances. The average value of the molecular depression of the *entire* series is as high as 1.85.[1] But the series comprises a large number of the *organic acids* which are known to be electrolytes.

*Omitting these*, since they have no right to be classed with the non-electrolytes, as everybody knows, the average value of the molecular depression of all the non-electrolytes examined by Raoult is 1.75, with aniline giving the value 1.53, and inverted sugar 1.93. This misrepresentation of Raoult's results is now quite general in the literature and for that reason I call attention to the matter.

More recent attempts to test the validity of the van't Hoff constant have been largely confined to ethyl alcohol, sugar and urea, which unfortunately constitute about the worst trio which could have been chosen for that purpose, since each presents an exception to the theory in question. Thus, sugar conforms to the theory only in solutions so dilute that the difficulty of determining the freezing point is very great. Ethyl alcohol does not conform to the theory at all, while urea seems to be so unstable in aqueous solutions that two attempts to repeat the work done by me on this compound in 1893 have been fruitless. For this reason no results for urea are found in the present paper.

[1] Ostwald's Chem., II., p. 751.

## DISCUSSION OF THE PRESENT RESULTS.

1. It is shown by the experimental results that a large number of widely different compounds in extreme dilution all have exactly *the same value for the molecular depression, namely 1.86.* This remarkable series comprises *n*-propyl alcohol, *n*-butyl alcohol, amyl alcohol, glycerine, acetone, dextrose, cane sugar, mannite and aniline.

The exceptions to this general conclusion are shown by

| | |
|---|---|
| Methyl Alcohol, | 1.82, |
| Ethyl Alcohol, | 1.84, |
| Ether, | 1.50. |

These exceptions are well established by the experimental results.

Thus the van't Hoff requirement that the molecular depression for non-electrolytes in great dilution should be constant is fulfilled in a large range of compounds, *with the constant value 1.86.*

It is to be observed that the formula given by van't Hoff required the value 1.89. But the factor 0.002 which the formula contained is now known to be too high. It should be, according to present knowledge, 0.00198. With this correction the value of the van't Hoff constant would be 1.87, while the present experimental results require it to be 1.86. I believe that it will be found that the value for $\lambda$, namely the heat equivalent of fusion for ice, which appears in the formula and to which van't Hoff assigned the value 79 as the most probable will be found by experiment to be 79.3 such at least is the value required by the experimental facts presented in this paper, provided the exact validity of the van't Hoff constant is allowed.

2. It appears as the concentration of the various solutions increases, the greatest diversity in the values of the molecular depression comes to light.

Thus, in the case of cane sugar, the molecular depression has rapidly increased to 1.98 at $m = 0.20$; in other cases it has shown little change; while in others, noticeably aniline, the molecular depression has fallen rapidly to 1.77 at $m = 0.20$. The significance of this change in the value of the molecular depression is evident when we remember that the van't Hoff equation is deduced on the as-

sumption that the dissolved substance behaves exactly as if it were in the state of an ideal gas with a volume equal to that of the solution. That is, it is assumed that the substance obeys the laws of Boyle and Gay Lussac *exactly*, which require $pv = RT$. Now no known gas does this perfectly. The familiar correction introduced by van der Waal by which the value of $v$ is so corrected as to make allowance for the space actually taken up by the molecules themselves is known to render the product $pv$ more nearly constant. The introduction of this correction in connection with a substance dissolved in any solvent is easily effected by defining the concentration of the solution not in terms of gram-molecules per 1000 cc. of the solution, but in gram-molecules per 1000 cc. of the *solvent* instead. This definition is the basis of the value, $m'$, given in column 5 of each table. By referring to the tables, under the heading $\triangle/m'$, it is found that the molecular depression has become constant in the case of methyl and ethyl alcohol, glycerine, dextrose, mannite and chloral hydrate. In the light of the van't Hoff theory this amounts to saying that these substances in aqueous solution behave exactly as if they were in the state of a gas.

In the remaining cases the application of this correction to $m$ does not suffice to render the molecular depression constant for all concentrations. In the case of sugar the correction seems to be too small to render the depressions constant, while in the rest of the cases this correction is too large to bring this about. The failure of this correction to bring the substances into accord with the requirement that they behave as gases is conspicuous in the case of aniline alone. It is the one case which I have examined where it seems possible to believe that the molecules of the dissolved substance combine themselves into molecular aggregates, more and more numerous in proportion as the concentration of the solution is increased. Anomalous as the aniline certainly is in the region of greater concentration it is the more important to observe that it is in exact accord with the demands of the theory when the dilution becomes extreme.

3. It will be remembered that the only exception to the general law that the molecular depression of non-electrolytes in *extreme dilution* is constant, was exhibited by methyl alcohol, ethyl alcohol

and ether. The exceptions here presented are pronounced and cannot possibly be explained by the assumption of unusual experimental errors. More experimental knowledge of these substances must be had before any explanation of their behavior in aqueous solution may be finally made. I wish merely to be permitted to suggest that the low values for methyl and ethyl alcohol is more than likely due to the fact that they evaporate rapidly from their aqueous solutions. To test this suspicion, I undertook to investigate the behavior of ether in this relation. The results confirm the suspicion, but exhibit an additional difficulty, namely, the values of the molecular depression are found not to increase or decrease uniformly with the increase in the concentration as is the case in the other compounds, but the change is according to a much more complex law. This appears best in the graphic representation. I have no explanation for this.

4. Before concluding this discussion of the results the important relation which they bear to the values found by the writer for the molecular depressions in the case of a large number of inorganic electrolytes must be pointed out. In general these values for the electrolytes have been about 2% lower than the dissociation theory of Arrhenius could account for. In making comparison between the experimental results and the requirements of this theory the van't Hoff constant plays a fundamental rôle, and I have always accepted the value 1.89 as the most probable theoretical value for this constant. According to the results of the present work it appears that this value is *too high* by 1.6%. Making use of the new value it turns out that the very large number of electrolytes which the author has examined are brought into full accord with this important generalization of Arrhenius.

## SUMMARY.

1. The method of determining the freezing points of dilute solutions introduced by the author in 1893 is shown to conform to the fundamental requirement of all exact cryroscopy, that the convergence temperature of the apparatus must be coincident with the *true freezing* point to be observed.

2. A source of error in the early practice of the method has

been discovered. This error arose from the fact that in order to keep the thermometer when not in use at the temperature of 0° C., the whole instrument was packed in ice. It is now known that only the lower part should be so treated, the upper part should be kept always at room temperature. This error is shown to account for the slight downward curvature which the graphic representation of the early results for the non-electrolytes.

3. The method is used to find the molecular depressions of a large number of other non-electrolytes in aqueous solution. It is found that the van't Hoff constant is exactly verified in all the cases examined except methyl alcohol, ethyl alcohol and ether. The experimental value is found to be 1.86.

In conclusion I wish to say that a few remaining non-electrolytes which should be investigated before a general conclusion may be drawn in regard to the validity of the van't Hoff constant will be studied as soon as the opportunity presents itself, and it is hoped that the additional knowledge so acquired may throw light upon the exceptions already found.

PRINCETON UNIVERSITY, July 5, 1899.

# AN ABSOLUTE DETERMINATION OF THE E.M.F. OF THE CLARK CELL.

BY HENRY S. CARHART AND KARL E. GUTHE.

A NEW determination of the electrochemical equivalent of silver was made a year ago by Patterson and Guthe[1]. The electrodynamometer employed for the purpose was fully described in their paper. Briefly a movable coil is suspended by a phosphorbronze wire approximately a meter long. The center of the movable coil is placed at the center of a fixed coil consisting of one layer of 576 turns of wire. The dimensions of both coils were intended to fulfill the requirements laid down by Andrew Gray[2] that the length should be as $\sqrt{3}$ to 1. The expression for the current is then

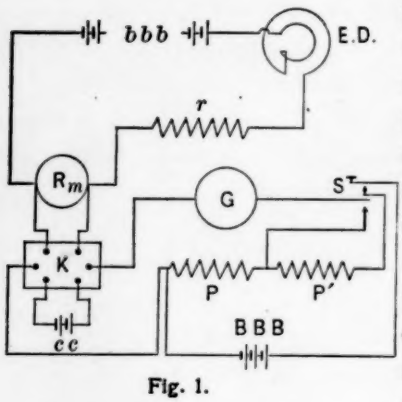


Fig. 1.

$$I = \frac{1}{Tr}\sqrt{\frac{2\pi K\sqrt{D^2 + L^2}}{Nn}}$$

for a twist of the wire through an angle $2\pi$. In this formula

$T$ is the period of vibration of a weight $M$ suspended by the phosphor-bronze wire.

$K$, the moment of inertia of the mass $M$.

$D$, the diameter of the fixed coil.

$L$, the length of the fixed coil.

$N$, the number of turns of wire on the fixed coil.

[1] PHYS. REV., Vol. VII., No. 39, Dec., 1898.

[2] Abs. Meas. in Electricity and Magnetism, Vol. II., p. 277.

$n$, the number of turns of wire on the movable coil.

$r$, the radius of the movable coil.

The electrochemical equivalent of silver found by Patterson and Guthe was 0.0011192 gm. per ampère per sec.

With such an instrument to measure the current, and with an appropriate coil of known resistance, it is obviously easy to compare the fall of potential of a measured current over this coil with the E. M. F. of a Clark standard cell. This work we have taken up the past year.

## The Clark Cells.

Two cells were made in accordance with the specifications legalized by act of Congress in 1894. They are of the Rayleigh H-form as modified by Kahle. One of them was made in the autumn of 1897 and the other in October, 1898. They do not differ more than one part in ten thousand. The negative consists of a zinc amalgam one part zinc to nine parts mercury. The mercurous sulphate was washed as directed in the legal specification, and the zinc sulphate was rendered neutral with zinc oxide. The amalgam and the mercurous sulphate are covered with crystals of zinc sulphate to a depth of about one cm.

Each cell is mounted in a case the top of which is fitted with a bayonet joint and is supplied with four legs. When the hard rubber top is removed it carries the cell with it. The legs serve for a support in a bath of petroleum. The temperature was taken by a thermometer graduated to fifths. It was made by Haak, of Jena, and has the certificate number 11021 of the Reichsanstalt. At 15° it reads 0.05° too low as certified by the Reichsanstalt.

## Method of Measurement.

The two Clark cells were connected in series. Their electromotive force was not balanced directly against the fall of potential over the manganin coil, but by Poggendorff's method the E. M. F. of the cells was first balanced against the fall of potential over a resistance $P$ in Fig. 1, and then the fall of potential over the manganin coil $R$ was balanced in the same way, while the current was adjusted so as to balance the torque of the phosphor-bronze wire of the electrodynamometer with a twist of one complete turn. Between

the resistance boxes $P$ and $P'$, each of 10,000 ohms, was placed a shunted Kohlrausch cylindrical bridge wire whose 1000 divisions had a resistance of 1.7 ohms. This arrangement enabled us to balance to fractions of an ohm. The resistance in this circuit was thus kept at 10,000 ohms plus the resistance of the shunted bridge wire, the contact on which was adjustable to secure a balance. The resistance $R$ over which the fall of potential was measured was the same manganin-coil used in the determination of the silver equivalent. The value was determined by comparison with two standard one-ohm coils made by Wolff in Berlin and tested by the Reichsanstalt. The certificates are numbered 160 and 163.

If $I$ is the current measured by the electrodynamometer, $E$ the E. M. F. of the two cells, $R_1$ the resistance in $P$ necessary to balance $E$, $R_2$ the resistance to balance the P. D. due to $I$, and $R$ the resistance of the manganin coil, then

$$E = RI\frac{R_1}{R_2}.$$

If $I$ be put equal to $a/T$, in which $a$ is made up of the constants in the expression for $I$ already given, then

$$E = R\frac{R_1}{R_2}\cdot\frac{a}{T}.$$

The axis of the movable coil was placed at right angles to the magnetic meridian to avoid dip. Moreover, it was necessary to reverse the current through the stationary coil without reversing through the suspended coil so as to eliminate a small disturbance due to the manner of leading in the current to the movable coil. Hence it was necessary to use all four permutations of direct and reversed currents through the two coils.

## DATA AND RESULTS.

The following table gives the resistances necessary for a balance by the Poggendorff method of comparison. In arrangement 2 the current was reversed through the movable coil without reversal through the fixed coil as compared with 1. $R_a$ is the resistance to balance with the current in one direction, $R_b$ the resistance to balance with the current reversed through the entire instrument, and $R_1$ the

resistance to balance the e. m. f. of the two standard cells. The column headed $t$ is the temperature of the phosphor-bronze wire.

TABLE I.

| Date. | Arrangement. | $R_a$ | $R_b$ | $R_1$ | $t$ | $T$ |
|---|---|---|---|---|---|---|
| May 27. | 1 | 7303.8 | 7299.0 | 4631.9 | 23.0° | 11.9850 |
| | 2 | 7422.25 | 7418.9 | 4631.9 | 23.4 | |
| " 30. | 1 | 7324.5 | 7320.0 | 4644.3 | 22.9 | 11.9847 |
| | 2 | 7443.0 | 7440.7 | 4644.3 | 23.2 | |
| " 31. | 1 | 7329.5 | 7323.7 | 4647.5 | 24.25 | 11.9875 |
| | 2 | 7449.4 | 7445.0 | 4647.5 | 24.2 | |

The value of the resistance $R$ to give a balance if there were no earth's field or asymmetry in the electrodynamometer would be very approximately $\sqrt{R_a' R_b' R_a'' R_b''}$, where the primes refer to arrangement 1 and the seconds to arrangement 2.

The resistance of the manganin coil was found to be 4.6304 ohms at 23°. Its temperature coefficient is very nearly zero at this temperature. Three comparisons were made with the Wolff coils by the Carey Foster method. Two additional English one-ohm coils were first compared with the German coils, and then all four in series with the manganin coil.

Referring again to the formula for the electromotive force,

$$E = R\frac{R_1}{R_2}\cdot\frac{a}{T},$$

we have to find the constant

$$a = \frac{1}{r}\sqrt{\frac{2\pi K\sqrt{D^2 + L^2}}{Nn}}.$$

The constants of the electrodynamometer in this formula are as follows:

$r$, 4.9968 cm.; $K$, 2251.89 cm².-gm.; $D$, 48.108 cm.;
$L$, 41.621 cm.; $N$, 576; $n$, 45.

The period of vibration of the weighted phosphor-bronze wire was determined at several temperatures just before its use in the electrodynamometer and again immediately afterwards. The period was slightly longer than it was a year ago, but the temperature co-

efficient was unchanged for the new temperature curve, Fig. 2, is parallel to the old one. It is highly probable that this wire has suffered some oxidation during the year.

The dimensions of both coils were measured over again. The movable coil had to be rewound, as the flattened copper wire was loose. The new dimensions are appreciably smaller than those for a year ago. The rubber continues to shrink somewhat, and it is proposed to try new materials for the purpose hereafter. The periods $T$ in the table are taken from the curve I, Fig. 2, at points

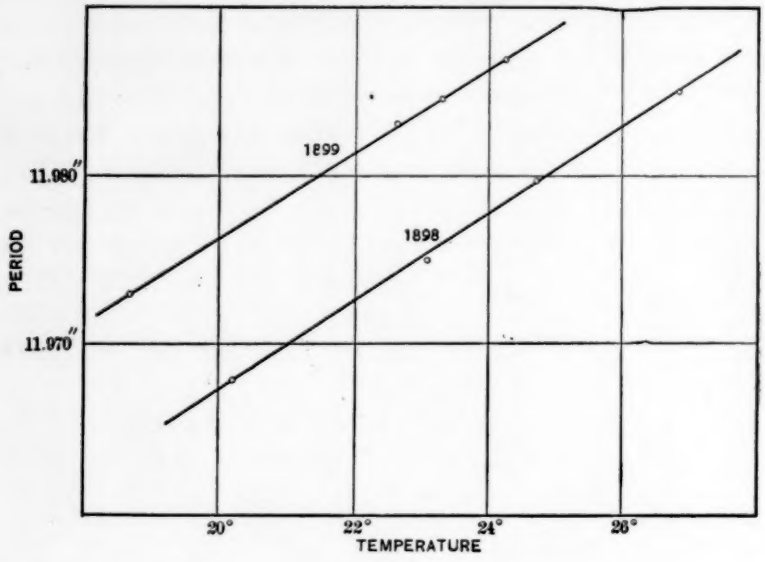



Fig. 2.

denoted by the mean temperatures. Substituting the numerical values we have the following results for the cells at the reading of 15° on the thermometer:

May 27, $E = 1.43355$ volts.
May 30, $E = 1.43333$ volts.
May 31, $E = 1.43305$ volts.

The dimensions of the movable coil were taken immediately after the last set of observations. Since it is known that its dimensions change by shrinking, and as a smaller value of $r$ increases the value

of the constant $a$, and hence the value of $E$, it is evident that any shrinkage between May 27 and May 31 tends to increase the value of $E$ from the first set of observations. We have accordingly thought best to give the first determination half the weight of the other two. The result, after correcting for the thermometer error of 0°.05, is

1.4333 volts at 15° C.

If we allow equal weights for the three determinations, the result differs by only one unit in the fourth decimal place. Since the two cells themselves differ by one part in ten thousand, and since we do not claim a degree of accuracy greater than one part in five thousand, the fourth decimal place is of course in doubt.

In 1892 Glazebrook and Skinner made a very careful determination of the E. M. F. of the Clark cell by the silver voltameter method, assuming 0.001118 as the silver equivalent. The result was 1.4342 at 15°.[1]

Kahle in 1898 found by means of a Helmholtz electrodynamometer the value for the modified H-form, 1.4328 at 15°.[2] But Kahle says that the silver equivalent for a solution neutralized with silver oxide is five parts in ten thousand higher than for a solution not so neutralized. He obtained for the silver equivalent 0.0011182. But neither he nor Glazebrook apparently neutralized with silver oxide. Hence if we employ 0.0011187 for a solution not neutralized by silver oxide and recalculate from Glazebrook's data, the result is 1.4332 at 15°. This is practically identical with ours.

PHYSICAL LABORATORY, UNIVERSITY OF MICHIGAN, July 10, 1899.

[1] Phil. Trans. (A), Vol. 183, p. 567, 1892.

[2] Zeitsch. f. Instrum. Kunde, June, 1898.

NOTE.—Since this paper was written the two Clark Cells used in the investigation have been taken by Professor Carhart to Berlin, and through the courtesy of the President of the Reichsanstalt, Professor Kohlrausch, of the Director of the technical department, Professor Hagen and of Professor Lindeck, the opportunity has been afforded of making several series of comparisons with the standards of the Reichsanstalt in Charlottenburg.

Unfortunately cell No. 2 was injured during the long journey, but No. 1 remained in good condition. No. 2 was often compared with No. 1 in Ann Arbor and was never more than one part in 10,000 lower than No. 1.

The result of three elaborate series of comparisons is that the E. M. F. of No. 1 is one part in 20,000 higher than the mean of all the normal Clark cells in both departments of the Reichsanstalt. This difference is well within the degree of accuracy attempted in this investigation.

# THE RESISTANCE OFFERED BY IRON WIRES TO ALTERNATING CURRENTS.

By Ernest Merritt.

THE abnormally large resistance offered by iron wires to alternating currents has been a matter of common observation for many years. The increased resistance is due to what is known as the "throttling effect," which prevents an alternating current from penetrating completely to the center of the wire; the effect is especially noticeable in iron because of the high permeability. The results of this throttling effect in the case of iron wires are sometimes quite startling, as for example in the case cited by Lord Kelvin, where the accidental short-circuiting of an alternating circuit by an iron bar caused the outer surface of the bar to be heated almost to redness, while the inner portions were scarcely warmed.

In the case of the non-magnetic metals, for which the permeability is constant, the computation of the resistance offered to alternating currents of a given frequency is a matter of no great difficulty. But in the case of iron the permeability changes with the current strength in accordance with a law that is as yet unknown. By assuming what appears to be a reasonable average value for $\mu$ and substituting this in the formula derived on the assumption of $\mu$ constant, we can obtain an approximate value for the resistance offered by an iron wire under given conditions; but, as I have pointed out in a previous article,[1] we have no means of telling how close this approximation will be. In fact it is questionable whether a formula derived upon the assumption of a constant permeability can be correct even in its general form; for it is to be remembered that the value of $\mu$ will not only change during the course of an alternation, but will also be different at a given instant in different parts of the wire, since the iron will be magnetized to a different extent at the surface from what it is at the center. The whole question is so

[1] The Distribution of Alternating Currents in Cylindrical Wires, Physical Review, Vol. 5, p. 47.

complicated that an experimental study of the subject seems necessary before correct conclusions can be reached.

The experiments described below were carried out at my suggestion by Mr. H. H. Denio,[1] to whose care and patience the consistent results are due. The method employed is open to criticism for several reasons, so that no high degree of accuracy can be claimed for the numerical values obtained. Nevertheless I think that the results will serve a useful purpose in calling attention to the more important peculiarities in the behavior of iron wires, and that they may be of assistance in planning a more accurate study of the phenomena.

The iron wire whose resistance was to be measured was made one arm of a Wheatstone Bridge, the other arm being formed by large wires of German silver. The wires were not coiled, but stretched between two heavy brass blocks, *AB* and *CD* (Fig. 1), these being mounted on a long board. The distance between *A* and *C* was 220 cm. The resistance of the German silver wire *BD* was about 0.5 ohm. Current, either alternating or direct as desired, entered the bridge at *AB* and *CD* and divided between the two branches in the ordinary way. The balance of the bridge was determined by means of a telephone, *T*, one of whose terminals was permanently connected to one end of the iron wire *MC*, while the other could be moved along *BD* until the sound in the telephone reached a minimum. Complete silence was never obtained.

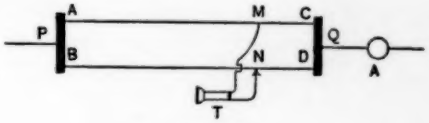


Fig. 1.

It was at first thought that the failure to obtain silence in the telephone was due to the fact that the inductance of *AC* was greater than that of *BD*. Several attempts were made to remove the difficulty by increasing the self induction of *BD*, but without success. I am now of the opinion that the trouble was caused by the variations occurring in the self induction of the iron wire during the course of an alternation. If this is true the difficulty is one that is inherent in the method.

[1] Thesis for the degree of B. S., 1898. Cornell Universty Library.

Although complete silence could not be obtained, it was always possible to set to a minimum of sound in the telephone with considerable certainty. A change in the quality of the sound in passing through the minimum often assisted in locating *N*.

The alternating current used had a frequency of about 130 periods per second.

It was expected that the resistance offered to alternating currents would depend upon the current strength. The current flowing in the iron wire was therefore varied through a wide range of values, the resistance being measured for each. Curves were then plotted showing the relation between current and resistance for each wire tested. The resistance for direct current was determined by the same apparatus. Since the current used was often strong enough to appreciably heat the wire, the measurements made with direct currents were also repeated with a number of different current strengths. The ratio of the alternating current resistance to the direct current resistance for the same current strength is then a

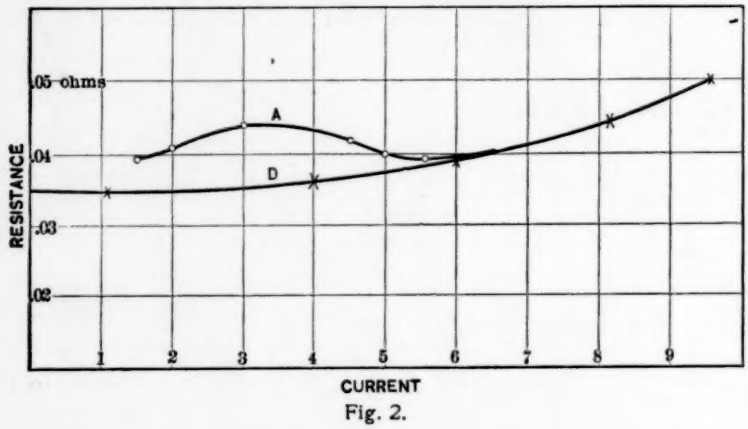



Fig. 2.

measure of the throttling effect. It will be observed that this method of procedure eliminates the errors that might arise from changes in resistance due to the heating of the wire.

Seven different wires were tested, ranging in diameter from 0.032 cm. to 0.476 cm. The curves shown in Fig. 2, which refer to a wire of 0.114 cm. in diameter, are typical of the behavior observed in all cases. The lower curve (*D*) shows the variation in

resistance with current strength as determined by using a direct current in the bridge. The increase in resistance in this case is due to the wire becoming heated. Curve *A* shows the resistance offered to alternating currents, also plotted as a function of the current strength. In Fig. 3 a similar set of curves is shown for a wire 0.366 cm. in diameter. With small current it was difficult to measure the resistance with accuracy, so that the portion of the curves near the origin are less reliable than those corresponding to larger currents.

In their general character the results represented by these curves are what might be anticipated from the known magnetic properties

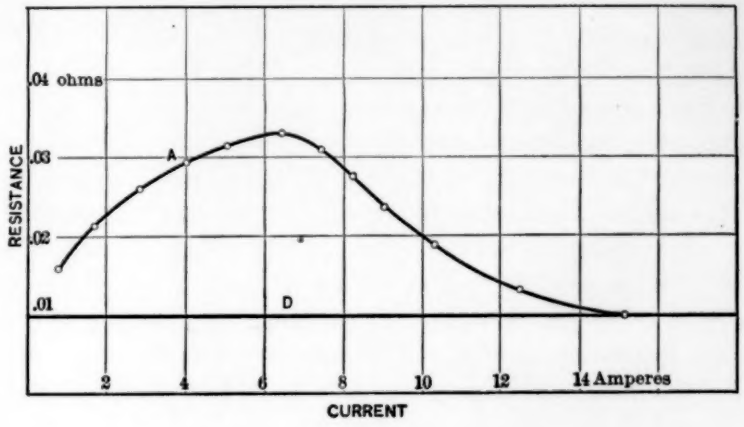



Fig. 3.

of iron. For small currents the iron is only weakly magnetized, so that its permeability is small. For such currents the behavior of the iron is therefore not very different from that of the non-magnetic metals, whose resistance, for the frequency and sizes of wire used, should be practically the same for alternating currents as for direct currents. As the current in the wire is increased the resulting magnetization becomes greater, and for a time the permeability rapidly increases. During the range of current values for which $\mu$ is large the throttling effect is well marked, the alternating current resistance being appreciably larger. The increase in resistance is of course greater for large wires than for small ones. If the current is increased still further, the outer layers of the wire begin to satu-

rate, and the permeability of this part of the iron is in consequence diminished. Roughly speaking, the wire is now equivalent to a core of high permeability, which is surrounded by a shell of practically non-magnetic material. The thickness of this saturated or non-magnetic layer increases with increasing current until finally the wire is saturated throughout, after which it again behaves like a non-magnetic substance and the resistance for alternating currents becomes appreciably the same as that for direct currents. The current for which the alternating current resistance is a maximum, as well as the relative value of this maximum resistance, will evidently depend upon the size and magnetic qualities of the wire.

A glance at the curves plotted in Figs. 2 and 3 shows that the results obtained by Mr. Denio are qualitatively the same as the above considerations would lead us to expect. Any quantitative test of these conclusions must of necessity be very incomplete. It is gratifying to observe, however, that the measured values of the alternating current resistance do not differ greatly from those resulting from an approximate theoretical treatment. In the case of the smaller wire, whose diameter was 0.114 cm., an alternating current of 3.5 ampères, corresponding to a maximum of about 5 ampères, would give $H = 18$ as the maximum magnetizing force at the surface. The average permeability of soft iron when carried through a cycle having this maximum magnetizing force is not far from 1000.[1] For the interior of the wire the value of $H$ would be less than 18 and permeability would therefore be somewhat larger. If we put the average permeability of the wire equal to 1600, the specific resistance being about 10,000, the ratio of the alternating current resistance to the ordinary resistance of the wire should be about 1.15. The observed value of this ratio, as shown by the curves in Fig. 2, was 1.34. The discrepancy between these two values, although considerable, is probably not greater than should be expected, for the computed value depends on the assumption of a *constant* permeability. For a current of 3.5 ampères the outer layers of the wire are already approaching saturation. For still larger currents the permeability would therefore be less than 1600, and we should expect the alternating current resistance to diminish with increasing

[1] Ewing, Magnetic Induction in Iron and other Metals, p. 107.

current. That this conclusion is verified by experiment is shown by the curve in Fig. 2.

A similar computation in the case of the larger wire (diameter = 0.366 cm.) shows that for a current of 7 ampères the alternating current resistance should exceed that for direct currents in the ratio of about 2.8 to 1. The value of this ratio determined by experiment was 3.2. But for a current of 7 ampères the magnetic force at the surface is only slightly greater than unity, so that saturation is not yet reached. The rapid decrease in resistance shown in Fig. 3 for larger currents is therefore hard to explain.

A number of other wires were tested, the results being in general more satisfactory with the wires of larger diameter. While the cases cited above are typical, it must be admitted that in some instances the quantitative agreement between observed and predicted results was even less satisfactory than in the case mentioned. Further experiments with more reliable methods will doubtless indicate more clearly in what way the approximate theory must be modified in order to become applicable to the magnetic metals.

# ON A THEOREM OF CLEBSCH'S.

BY PAUL SAUREL.

CLEBSCH has shown[1] that the integrals of the equations of motion of a vibrating elastic solid can be put into a very simple and elegant form. His demonstration, while by no means long or difficult, seems, nevertheless, to admit of some simplification.

The equations in question are :[2]

$$\left.\begin{aligned} \frac{\partial^2 u}{\partial t^2} &= a^2 \Delta u + (b^2 - a^2)\frac{\partial \sigma}{\partial x} \\ \frac{d^2 v}{\partial t^2} &= a^2 \Delta v + (b^2 - a^2)\frac{\partial \sigma}{\partial y} \\ \frac{\partial^2 w}{\partial t^2} &= a^2 \Delta w + (b^2 - a^2)\frac{\partial \sigma}{\partial z} \end{aligned}\right\}, \qquad 1$$

in which

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

and

$$\sigma = \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}.$$

From the above equations, it follows without difficulty that

$$\frac{\partial^2 \sigma}{\partial t^2} = b^2 \Delta \sigma. \qquad 2$$

Let $u$, $v$, $w$ be any given solution of the above equations and let us write

$$\left.\begin{aligned} u &= \frac{\partial P}{\partial x} + u' \\ v &= \frac{\partial P}{\partial y} + v' \\ w &+ \frac{\partial P}{\partial z} + w' \end{aligned}\right\}. \qquad 3$$

[1] Clebsch, Ueber die Reflexion an einer Kugelfläche. Borchardt's Journal für die reine u. angew Math., Bd. 61.

[2] Kirchhoff, Vorlesungen über Mechanik, XI Vorlesung.

From these we obtain

$$\sigma = \Delta P + \sigma' \qquad 4$$

in which $$\sigma' = \frac{\partial u'}{\partial x} + \frac{\partial v'}{\partial y} + \frac{\partial w'}{\partial z}.$$

If we substitute the above values of $u$, $v$, $w$ in the equations of motion, we get

$$\left.\begin{aligned} \frac{\partial^2 u'}{\partial t^2} + \frac{\partial}{\partial x}\left[\frac{\partial^2 P}{\partial t^2} - b^2 \Delta P\right] &= a^2 \Delta u' + (b^2 - a^2)\frac{\partial \sigma'}{\partial x} \\ \frac{\partial^2 v'}{\partial t^2} + \frac{\partial}{\partial y}\left[\frac{\partial^2 P}{\partial t^2} - b^2 \Delta P\right] &= a^2 \Delta v' + (b^2 - a^2)\frac{\partial \sigma'}{\partial y} \\ \frac{\partial^2 w'}{\partial t^2} + \frac{\partial}{\partial z}\left[\frac{\partial^2 P}{\partial t^2} - b^2 \Delta P\right] &= a^2 \Delta w' + (b^2 - a^2)\frac{\partial \sigma'}{\partial z} \end{aligned}\right\} \qquad 5$$

Suppose that $$\sigma' = 0. \qquad 6$$

The necessary and sufficient condition for this, is (equation 4) that

$$\Delta P = \sigma. \qquad 7$$

Suppose moreover that $P$ satisfies the equation

$$\frac{\partial^2 P}{\partial t^2} = b^2 \Delta P. \qquad 8$$

Equations 5 then become

$$\left.\begin{aligned} \frac{\partial^2 u'}{\partial t^2} &= a^2 \Delta u' \\ \frac{\partial^2 v'}{\partial t^2} &= a^2 \Delta v' \\ \frac{\partial^2 w'}{\partial t^2} &= a^2 \Delta w' \end{aligned}\right\} \qquad 9$$

If, then, it be possible to choose $P$ so that equations 7 and 8 are simultaneously verified, equations 3 will determine $u'$, $v'$, $w'$. We shall thus have established that every solution of the given equations can be written in the form of equations 3, $P$ being a common integral of equations 7 and 8, and $u'$, $v'$ $w'$ being three solutions of the equation

$$\frac{\partial^2 \varphi}{\partial t^2} = a^2 \Delta \varphi, \qquad 10$$

these solutions, moreover, being connected by equation 6:

$$\frac{\partial u'}{\partial x}+\frac{\partial v'}{\partial y}+\frac{\partial w'}{\partial z}=0. \qquad 11$$

In order to show that we can determine $P$ so as to satisfy equations 7 and 8, let us write the equation obtained from them:

$$\frac{\partial^2 P}{\partial t^2}=b^2\sigma. \qquad 12$$

The pair of equations 7 and 8 may be replaced by the pair of equivalent equations 7 and 12. The integral of equation 12 is

$$P=b^2\int dt\int\sigma dt+A(x,y,z)\cdot t+B(x,y,z),$$

$A$ and $B$ being two arbitrary functions. From this equation we obtain

$$\Delta P=b^2\int dt\int\Delta\sigma dt+\Delta A(x,y,z)\cdot t+\Delta B(z,y,z).$$

Choosing the arbitrary functions so that

$$\Delta A(x,y,z)=0,\quad \Delta B(x,y,z)=0$$

and making use of equation 2, we obtain

$$\Delta P=\int dt\int\frac{\partial^2\sigma}{\partial t^2}dt=\sigma.$$

Thus equation 7 is also verified and the theorem stated above is established.

This result may be put into a more striking form if we make use of a theorem tacitly admitted by Clebsch and rigorously established by Duhem.[1] The theorem in question is the following: If $u'$, $v'$, $w'$ are three integrals of equation 10, which also verify equation 11, we may write

$$u'=\frac{\partial W}{\partial y}-\frac{\partial V}{\partial z},$$
$$v'=\frac{\partial U}{\partial z}-\frac{\partial W}{\partial x},$$
$$w'=\frac{\partial V}{\partial x}-\frac{\partial U}{\partial y},$$

in which $U$, $V$, $W$ are three solutions of equation 10.

[1] Duhem, Sur l'intégrale des équations des petits mouvements d'un solide isotrope. Mémoires de la Société des Sciences de Bordeaux. 5e Série, t. III., p. 325, 1899.

Thus finally we obtain Clebsch's theorem: Every solution of the equations of motion of a vibrating elastic solid can be written in the form:

$$\left.\begin{aligned} u &= \frac{\partial P}{\partial x} + \frac{\partial W}{\partial y} - \frac{\partial V}{\partial z} \\ v &= \frac{\partial P}{\partial y} + \frac{\partial U}{\partial z} - \frac{\partial W}{\partial x} \\ w &= \frac{\partial P}{\partial z} + \frac{\partial V}{\partial x} - \frac{\partial U}{\partial y} \end{aligned}\right\}, \qquad 13$$

$U$, $V$, $W$ being three solutions of the equation

$$\frac{\partial^2 \varphi}{\partial t^2} = a^2 \Delta \varphi \qquad 14$$

and $P$ being a solution common to the equations

$$\frac{\partial^2 P}{\partial t^2} = b^2 \Delta P \qquad 15$$
$$\Delta P = \sigma.$$

Conversely, if $U$, $V$, $W$ are any three solutions of equation 14, and $P$ any solution of equation 15, equations 13 furnish a solution of the equations of motion. This is very easily verified by substituting in the original equations the values of $u$, $v$, $w$ given by equations 13.

BORDEAUX, April, 1899.

# AN INVESTIGATION OF THE MAGNETIC QUALITIES OF BUILDING BRICK.

O. A. GAGE AND H. E. LAWRENCE.

THE magnetic disturbances existing in physical laboratories have in a few cases, been traced to the brick work of the walls and piers of the building. Having in mind the selection of a brick suitable for a laboratory of physics, it became desirable to investigate, so far as possible, the causes and behavior of the magnetism known to exist in some building bricks. For this purpose samples were furnished the writer from many of the factories of the northern and eastern states. These included all varieties of shades of color of which an attempt is made to convey an idea to the reader in the accompanying tables. The greater number were of the pressed brick variety, though specimens of the ordinary red variety are included. In all the samples but one—number 24, nearly white in color—magnetism was found to a greater or less degree.

The apparatus used was a magnetometer of the ordinary "end-on" form, constructed for the purpose, the telescope being mounted at a distance of about 125 cm., the center of the brick when in position being about 14 cm. from the magnetometer needle. The position of the poles was found approximately by presenting the different faces in turn to the magnetometer; the two opposite causing the greatest deflection were said to contain the poles. In all cases these were found to be either in the faces or edges, never in the ends of the bricks. This position was permanent and could not be changed by any means at hand.

The opposite table gives the results first obtained on thirty-one samples.

Although a large number of the same kind was not examined, yet in a few cases duplicates are included. Nos. 5, 9, 10, 11, 12 are alike and their moments, 0.330, 0.256, 0.256, 0.282, 0.209, re-

| Brick. | Color. | Deflection. | Angle of Deflection. | Moment. | Position of Poles. |
|---|---|---|---|---|---|
| 1 | Ordinary Red. | 0.9 | 17′14″ | 0.924 | Edge. |
| 2 | " " | 0.55 | 10 32 | 0.565 | " |
| 3 | " " | 0.575 | 11 1 | 0.591 | " |
| 4 | " " | 0.475 | 9 6 | 0.495 | " |
| 5 | Pressed " | 0.3 | 5 45 | 0.330 | " |
| 6 | Cream. | 0.5 | 9 35 | 0.558 | " |
| 7 | Brown. | 2.25 | 43 5 | 2.476 | " |
| 8 | Pressed Red. | 0.55 | 10 32 | 0.573 | " |
| 9 | " " | 0.25 | 4 47 | 0.256 | " |
| 10 | " " | 0.25 | 4 47 | 0.256 | " |
| 11 | " " | 0.3 | 5 45 | 0.282 | " |
| 12 | " " | 0.2 | 3 50 | 0.209 | " |
| 13 | Brown. | 1.0 | 19 9 | 1.116 | " |
| 14 | " | 1.05 | 20 7 | 1.172 | " |
| 15 | " | 1.05 | 20 7 | 0.821 | Face. |
| 16 | Brown Spotted. | 0.35 | 6 42 | 0.362 | Edge. |
| 17 | " " | 0.2 | 3 50 | 0.206 | " |
| 18 | " " | 0.3 | 5 45 | 0.308 | " |
| 19 | Cream. | 0.15 | 2 52 | 0.160 | " |
| 20 | " | 0.3 | 5 45 | 0.326 | " |
| 21 | Red Spotted. | 0.3 | 5 45 | 0.326 | " |
| 22 | " " | 0.1 | 1 55 | 0.078 | Face. |
| 23 | Cream Spotted. | 0.1 | 1 55 | 0.109 | Edge. |
| 24 | White. | 0.000 | | 0.000 | |
| 25 | Pressed Red. | 3.0 | 57 26 | 2.428 | Face. |
| 26 | " " | 2.65 | 50 44 | 2.070 | " |
| 27 | " " | 2.55 | 48 50 | 1.992 | " |
| 28 | White. | 0.05 | 0 53 | 0.035 | " |
| 29 | " | 0.05 | 0 53 | 0.035 | " |
| 30 | " | 0.05 | 0 53 | 0.049 | Edge. |
| 31 | " | 0.05 | 0 53 | 0.049 | " |
| 32 | " | 1.00 | 19 9 | 0.997 | " |

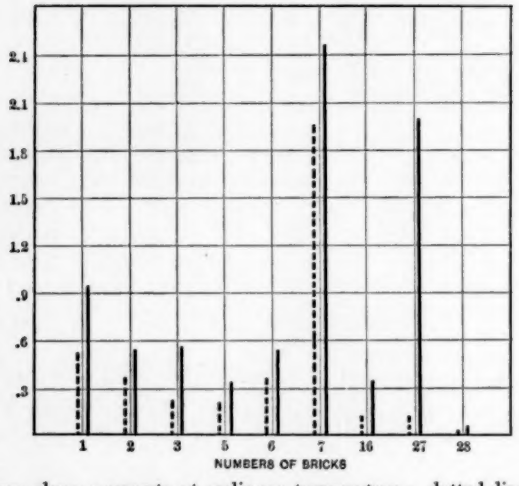
spectively, show no great variation. The bricks in each of the following series are alike: Nos. 13, 14, 15; Nos. 16, 17, 18; Nos. 25, 26, 27; Nos. 24, 28, 29, 30, 31; the moments of those belonging to the some set being fairly equal in view of the variable composition of the brick.

The moments of the bricks are not constant. The foregoing readings were taken in October, 1898. The experiments were resumed in January, 1899. The following table gives the measurements taken then:

| Brick. | Deflection. | Moment. | |
|---|---|---|---|
| | | Oct., '98. | Jan., '99. |
| 2. | 0.55 | 0.565 | 0.565 |
| 3. | 0.5 | 0.591 | 0.513 |
| 5. | 0.7 | 0.330 | 0.770 |
| 6. | 1.4 | 0.558 | 1.562 |
| 7. | 14.62 | 2.476 | 15.994 |
| 8. | 0.4 | 0.573 | 0.416 |
| 16. | 0.1 | 0.362 | 0.103 |
| 20. | 0.2 | 0.326 | 0.217 |
| 21. | 0.1 | 0 326 | 0.107 |
| 23. | 0.8 | 0.109 | 0.868 |
| 25. | 3.0 | 2.428 | 2.428 |
| 27. | 2.3 | 1.992 | 1.797 |
| 28. | 0.1 | 0.035 | 0.076 |

It will be noticed that the bricks did not vary in the same direction, some increasing, others decreasing in strength.

No good idea of the strength of the brick can be obtained from the value of its moment; but when compared with a steel magnet,




Black lines show moments at ordinary temperature; dotted lines show the same when heated.

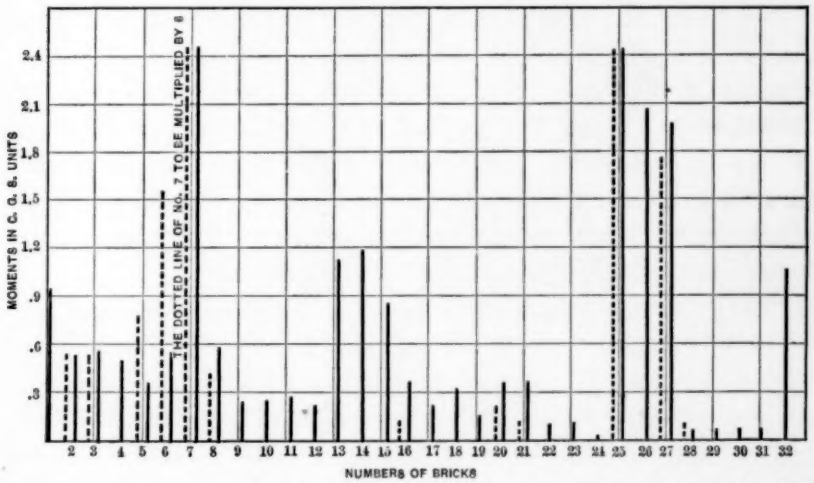
its force is better apprehended. Assuming that the steel magnet has 0.325 c. g. s. units to the cubic millimeter, brick No. 7 at its first strength would be equivalent to a steel magnet 9.7 mm. in length and 1 mm. in diameter; at its new strength, to a magnet 62.7

mm. in length and 1 mm. in diameter. Brick No. 1 would equal a similar magnet 3.53 mm. in length.

The moments of the bricks were changed when rapped in the field of a motor and also when heated. The temperature to which they were heated was low; but, nevertheless, the diminution of the moments was in all cases marked, and, in some, extraordinary. In all cases the bricks regained their strength upon cooling. The results obtained are tabulated and shown below.

| Brick. | Deflection. | Temperature. | Moment. | | Ratio. | |
|---|---|---|---|---|---|---|
| | | | Hot. | Cold. | Cool. | Hot. |
| 1. | 0.55 | 110°C. | 0.56 | 0.92 | 1 | 0.61 |
| 2. | 0.35 | 130 | 0.36 | 0.56 | 1 | 0.64 |
| 3. | 0.25 | 130 | 0.26 | 0.59 | 1 | 0.44 |
| 5. | 0.2 | 140 | 0.22 | 0.33 | 1 | 0.67 |
| 6. | 0.325 | 110 | 0.36 | 0.56 | 1 | 0.64 |
| 7. | 1.8 | 130 | 1.98 | 2.48 | 1 | 0.80 |
| 16. | 0.15 | 140 | 0.15 | 0.36 | 1 | 0.42 |
| 27. | 0.15 | 130 | 0.12 | 1.99 | 1 | 0.06 |
| 28. | 0.00 | 130 | 0.00 | 0.04 | | |

An interesting point in this variation is the ratio at which the various bricks diminish in strength. If the bricks containing the same clay had been used, the constancy of the ratio would not be




Black lines show moments in October, 1895; dotted lines show the same in January, 1899.

surprising; but when bricks, quite different in composition, lose their magnetism so uniformly, it is certainly strange. Omitting bricks Nos. 27 and 28, the average of the ratio is 1 : 0.6 and four of these differ very slightly from the mean.

The bricks were also tested for permeability. The magnetometer method was used and in the first coil the wire was wound perpendicular to the long axis of the brick and consisted of 185 turns. Accordingly, the magnetic axes of the brick and the coil were at right angles. In a second coil of 125 turns, the magnetic axis was parallel to that of the brick. The coils were so wound that the brick could be removed, and its permeability was tested by noting whether its presence or absence produced any effect upon the magnetometer needle. Currents as large as four ampères were used, yet the bricks apparently had no effect upon the strength of the coils.

No experiments were performed to prove directly the cause of the magnetism; but, in the course of some previous ones, light was thrown upon the subject. The greater part of the magnetism is probably due to the presence of the magnetic iron oxide, for the powder from several of the bricks gave up small particles to the magnet, and iron is the only constituent of the clays that would act this way. Also, the larger amount of iron oxide in a clay makes the brick more magnetic, other things being equal. Thus brick No. 25 contains about five times as much iron as No. 28 and is very much stronger. Brick No. 6 contains about the same amount of iron as No. 25, but is not nearly so strong. This may be due to the fact that No. 6 has over 14% of lime and 4% of magnesium, while No. 25 has no lime and only 0.5% of magnesium. The iron is supposed to form double silicates of lime and iron similar to the mineral zoisite, and, in this form, the iron is probably non-magnetic. Nos. 1 and 3 are also stronger than 6 when they contain less iron and also less lime and magnesium.

The permanent magnetism is probably due to the cooling of the bricks in the magnetic field of the earth. One or two facts seem to support this theory. The position of the poles was somewhat remarkable in that it was never found in the head of the brick. This may be explained by the way in which they are placed in the kilns to be burned. They are placed always on the face or edge allowing the

magnetic lines of the earth to pass through either both faces or both edges. No direct proof of this was obtained, but one brick similar to No. 1 of the ordinary red variety, which had not been burned, was tested and contained no magnetism. Accordingly, it may be that burning is the agent which gives the bricks their permanent magnetism.

To recapitulate, the bricks were, in most cases, found to be permanent magnets of slight and varying strength. The magnetism was affected by heat and strong magnetic fields. The probable cause is the presence of magnetic iron oxide, either a constituent of the clay or formed by heat.

## NOTE.

*Robert Wilhelm Bunsen.*—By the death of Professor Bunsen, who passed away at a ripe old age, in Heidelberg, on the 15th of August, chemistry and physics lose one of the most gifted men who ever devoted his life to their advancement. It would indeed be difficult to say which of these two sciences owes most to him.

Bunsen was born in Göttingen on March 25, 1811, where his father was professor of theology. Born and brought up in academic circles, he completed his schooling early. He received his doctor's degree in the University of his native city in 1830 and it was in that institution, in 1833, that he began his career as privatdocent. In 1836 he was appointed to the professorship of chemistry in the polytechnic school at Cassel, and in 1838 to a similar chair in the University of Marburg, which position he filled for thirteen years. In 1851 he was appointed professor of chemistry at Breslau and in the following year accepted the chair in that science at Heidelberg, which he filled up to the time of his retirement, after more than forty years of active service.

In reviewing Bunsen's work, one is struck with the importance of much of it, considered from a strictly utilitarian point of view. His was, however, a utilitarianism which never developed into commercialism. No man was ever a more staunch adherent to the cause of pure science than Bunsen, and while he turned out one useful device after another, with a fertility and ingenuity which would have made his fortune, had he turned his attention to industrial pursuits, he showed not the slightest tendency to forsake the high calling of a scientific investigator for that of the inventor. So far, indeed, was his nature free from worldliness that he was one of the few eminent men of science in all Germany who, during the rush to the great centers during the early years of the empire, was not to be coaxed from his quiet life in a small university town. In Heidelberg, the scene of his most important scientific achievements, he died as he had lived, a simple German University professor of the old school.

The first piece of work published by Bunsen after his graduation from the university, is characteristic of the intense interest which he always had in the practical as well as the purely scientific aspects of a subject. It dealt with the remarkable properties of freshly prepared ferric hydroxid as an antidote for arsenical poisoning. It was a discovery of genuine importance, for this material has since been the standard remedy in such cases, and has been the means of saving many lives. In the following

year, 1835, he began his well-known experiments upon the double cyanides, and in 1837 he laid the foundation of an important branch of chemistry, that of the organic compound radicals. His discovery of cacodyl ($C_2H_6As$) and his investigations of the remarkable properties of its highly poisonous, inflammable and explosive compounds, forms one of the most fascinating chapters in the history of science. Roscoe in his account of the early work of Bunsen, written for *Nature* in 1881, compared his experience in this exploration to that of a traveler "in an unknown and treacherous land, without sign posts to guide him, or more assistance on his travels than was furnished by his own scientific acumen and his unfaltering determination." In the course of this work he had one eye blinded by an explosion, and very nearly lost his life by breathing the poisonous vapors.

Bunsen's memoir upon this subject was published in 1837, and he almost immediately turned his attention to the investigation of the gases given off by blast furnaces, in the course of which he was led to the development of the methods of gas analysis, which were brought together many years later, in his famous treatise entitled *Gasometrische Methoden.* The methods of manipulation employed in this work are those of the physicist, and it is probably due to his experience with them that Bunsen was turned from the domain of pure chemistry to the middle ground of chemical physics, in which he was one of the chief investigators of his time.

It is with his contributions to the science of physics that we have to do in this notice, and it is possible in considering simply this phase of his scientific activity to do little more than to mention the succession of important contributions which we owe to him. In 1841 he invented the Bunsen battery, in which carbon was substituted for the platinum as the negative pole of the voltaic cell. From 1843, when his last paper on this subject appeared, until 1847, was a period of quiescence. In the latter year he visited Iceland, and one of the results of this visit was his theory of the geyser, together with the classical experiments by means of which he imitated, artificially, its action and verified his views of the phenomena. These studies were followed in 1854 by the production of chromium and other metals by electrolysis. In 1857, with the colaboration of Roscoe, he completed his remarkable photochemical studies; in the course of which the action of light in bringing about the union of hydrogen and chlorine, was exhaustively investigated.

About 1860 Bunson formed a scientific partnership with his friend and colleague, Gustav Kirchoff, then professor of physics in Heidelberg, which was to result in the most brilliant achievement of his own scientific career, probably of the decade. This was the application of the study of the spectrum to chemical analysis, and the extension of such analysis by the identification of the black lines in the solar spectrum with the bright lines found in the spectra of metals, to solar and stellar

atmospheres. One of the fruits of this investigation was the discovery of cæsium and rubidium by means of their spectra, a performance which, taken by itself, would have sufficed to have stamped the work as of the highest importance to both physicists and chemists.

The last really important work published by Bunsen is contained in his paper entitled "Calometrische Untersuchungen" (*Poggendorf's Annalen*, vol. 14, 1870). It was in this paper that his well-known ice calorimeter is described, an instrument which, in the hands of its inventor, gave results of a degree of delicacy hitherto unattained in calorimetric work, and made it possible to determine with accuracy the specific heats of materials of which only very small quantities were available. For several years, indeed, he continued to contribute to the *Annalen*, publishing several papers on spectrum analysis, and exhibiting in 1883 a quality which had always characterized his scientific work, that of attention to minute detail, in his study on the progressive condensation of carbonic acid on glass surfaces. In the heated discussion which followed upon this subject between himself and Kayser, Bunsen showed that he was still able to defend his views vigorously, and to verify his conclusions by experimental work of the most delicate and trying character. His final contribution, a paper on the steam calorimeter, was published in the *Annalen* in the year 1887.

For several years after his scientific career, lasting nearly forty years, was ended, Bunsen, continued to be a figure on the streets of Heidel berg. Gradually, as old age came upon him, he retired more and more from the public life of the university town, where for half a century he had been the most notable character, and finally, in his eighty-ninth year, passed peacefully away.

Bunsen was no less eminent as a teacher than as an investigator. A generation of chemists, not only in Germany, but in England and in America, and many students in physics likewise, look back with gratitude to the days which they spent in his laboratory. His domain was a middle ground between the two sciences. A chemist by training, his greatest contributions to that science arose from his application to one field of research after another, of the methods of physics.

Of the numerous appliances which our laboratories owe to his ingenuity, the Bunsen burner, the Bunsen filtering pump, the Bunsen spectroscope, the Bunsen photometer and the Bunsen calorimeter, are perhaps the best known. These remain to remind us that Bunsen was not only a chemist and physicist, but he had in him the essentials of a successful inventor. Science owes him a debt of gratitude in that he did not yield to the temptation to enter upon purely an industrial field, but gave himself, from the beginning of his life to the end of it, solely to her service.

E. L. N.

## NEW BOOKS.

*A Text-book of General Physics.* By CHARLES S. HASTINGS and FREDERICK E. BEACH. Pp. viii + 768. Boston, Ginn & Company, 1899.

The evolution of the modern text-book of physics has been a rapid one.

Thirty years ago we were still under the influence of the age of the discoverer and pioneer, the age of Davy and Faraday and Henry. Natural philosophy, to use the good old name, was still a wonderland to be exploited, and its attitude toward nature was still mainly descriptive. Phenomena were the principal thing, and the theoretical thread connecting them, in the elementary text-book, was but slender. For the general student, the great structures of modern physical theory still lay concealed in the mathematical formulæ of their first expositors. The order of treatment, as was natural, was historical, rather than logically progressive.

The introduction of laboratory methods, the spread of mathematical physics, the growth of the elective system in colleges, and the rise of the graduate schools made demands on elementary instruction that the text-books of the day could not supply. The laboratory demanded quantitative statements of relations, which could be tested by experiment. The advanced courses required a logical introduction, a firm grasp of definitions, a compendium, in short, of the elements on which physical theory is founded.

Thus mechanics, which thirty years ago was by many teachers of physics hardly touched upon in the college course, now underlies everything, and the aim even in the elementary text-book has become, not the description of phenomena, but the application of mechanical principles in all branches of the science. Meanwhile the enormous growth of the whole subject makes it necessary to narrow still more the range of phenomena described, so that elementary physics, in many modern text-books, has come to be treated entirely as a discipline, the chief aim of which is to train for the more advanced courses.

The progress in the treatment of the subject has been great, yet not without loss. The text-books of the day have become abstract, general and, in some cases, to the ordinary student, dry. The deductive side of physics has crowded out the experimental and the phenomenal, which really are the foundations. These remain, of course, in the laboratory, but the subjects which can be there introduced are few and simple.

For these reasons a book like the present one, which has to some extent the characteristics of the older type, or represents, as perhaps we

should rather say a return of the pendulum which had swung too far, is to be welcomed. It is however not reactionary, but distinctly modern in its attitude. Theoretical discussion holds the first place, and is in fact in some cases carried to such detail as to be of questionable value in a general text-book. Descriptions of apparatus and phenomena are introduced chiefly for the illustration and application of theoretical principles. Mechanics is very fully treated, as the authors themselves remark, as the foundation of the whole science, and fully illustrated.

The discussion of circular motion affords an excellent illustration of the method of the book.

After an extended and rather fresh discussion leading to the usual equations, no less than fifteen different applications of the principle are taken up in detail including the conical pendulum, both in its simple form, and that more commonly used in chronographs and driving clocks, such machines as the centrifugual dryer and the cream separator, the gyroscope in two forms, and a variety of meteorological and astronomical problems depending on the rotation of the earth. Not only is the application of the principle in various ways thus clearly shown, but its importance in Nature is emphasized. The use of similar methods throughout the book leads to long discussions on special topics. These are always topics which by their intrinsic interest, and their wide applications to natural phenomena offer themselves easily to such treatment. Thus surface tension, the theory of solutions, the kinetic theory of gases, thermodynamics, wave-motion, are treated at unusual length and in a highly interesting manner.

The treatment of acoustics, following the chapter on wave-motion, is excellent, especially in its relations to music and musical instruments.

The chapters on electricity are less satisfactory. Many fundamental propositions are assumed without proof (as potential at a point, magnetic induction, hysteresis, the equivalence of a circuit and a magnetic shell) and so much ground is covered, so many subjects briefly touched, that the general impression is of confusion and overcrowding of material, and lack of assimilation of the parts. Some discussions would be practically unintelligible to a student from lack of previous definition of terms, as, for example, the introduction of "Faraday tubes" on page 510.

The subject of optics, on the other hand, is admirably handled, the portion on optical instruments especially so. The "wave-front" method of discussion is adopted from the beginning and is applied to the ordinary problems of reflection and refraction in a concise and elegant manner. There is a welcome chapter on the optical phenomena of the atmosphere, a subject too frequently ignored in text-books. The section on color-vision is clear and careful, though it must be said that the Young-Helmholtz theory cannot be trusted even to the extent to which the authors

carry it to explain the phenomena of color-vision, and the insufficiencies pointed out by them are by no means the only ones.

The method of the book requires space, and the amount of material is considerably greater than in most of the more modern class-books, though not approaching the encyclopædic dimensions of some of the older treatises. The illustrations in the text are supplemented by a large number of well-selected problems at the end of each chapter.

The mechanical execution of the work is excellent, and but few slips, either of printing or in statement, have been noted. The book is a valuable addition to the college text-books now available.

FRANK P. WHITMAN.

*Practical Physics.* By WILLIAM WATSON. pp. xvi+238. London and New York, Longmans, Green & Co., 1896.

This useful little laboratory manual contains one hundred and ninety-three exercises for experiments in elementary physics. These are nearly all quantitative in character, and are designed to be carried out with the use of simple forms of apparatus. There are thirty-one experiments in simple mensuration, including the measurements of lines and of surfaces and of mass, volume and density. Hydrostatics and exercises upon the properties of gases precede the work upon mechanics of solids, which is an unusual arrangement of subjects. A short but very good section upon the geometrical representation of varying quantities deals with the use of cross section paper in the plotting of curves. The selection of material is almost always excellent.

The relation of the metric system to British measures is dealt with at the beginning of the volume and thereafter the metric system is used with a fair degree of consistency throughout. It is to be noted, however, as in many works written by those who have been brought up to the use of British measures, that these are employed in many instances in the description of apparatus. An example of this occurs in Exercise 78, entitled "Motion on an Inclined Plane," which reads as follows: "*Apparatus: Smooth board, about 6 feet long, and 6 or 8 inches wide; a long wedge about 3 inches thick at the wide end; . . . . Place the wedge under one end of the board so that this end is about one inch higher than the other. At about two inches from the higher end, draw a line across the board at right angles to the length, etc.*" In making measurements with this apparatus, however, centimeters are again employed. It is obvious that the author, like many other working physicists, still does his *thinking* in terms of the British units and that the use of the metric system is an artificial matter with him. It will continue to be so with students and teachers unless the writers of manuals and the directors of laboratories make it a practice to deal in the metric system to the rigorous exclusion of all others.

E. L. N.

*Harper's Scientific Memoirs: The Laws of Gases.* Memoir by ROBERT BOYLE and E. H. AMAGAT. Translated and edited by CARL BARUS.

*The Second Law of Thermodynamics.* Memoirs by CARNOT, CLAUSIUS and THOMSON. Translated and edited by W. F. MAGIE.

*The Fundamental Laws of Electrolytic Conduction.* Memoirs by HITTORF and F. KOHLRAUSCH. Translated and edited by H. M. GOODWIN. New York, 1899.

No more fortunate selection could have been made for the fourth volume of this series than the translation of Amagat's celebrated papers on the *Compressibility of Gases at High Pressure* for as the translator, Professor Carl Barus, says in his terse but pointed preface, everybody cannot so easily get these papers into his possession.

Amagat's memoirs belong to the class of scientific literature which one would like to have at his elbow, and the scientific men of America are indebted to Professor Barus for making this possible.

One cannot say as much for the materials contained in the volume on the "Second Law of Thermodynamics." Since an excellent American translation of Sadi Carnot's *Memoir on the Motive Power of Heat* has recently been published, and since Kelvin's paper on the *Dynamical Theory* has likewise been rescued from its hiding place in the transactions of the Royal Society of Edinburgh, and has been incorporated in volume I. of his *Mathematical and Physical Papers*, there would seem to be little occasion for the reprinting of either. As to the celebrated paper by Clausius, which is inserted between the translation of Carnot, and the reprint of Kelvin in this volume, that likewise can be regarded as reasonably accessible to the student of physics. It appeared in the Berlin Academy, February, 1850, was reprinted in Poggendorff's Annalen of that year, volume 79, was translated in the *Philosophical Magazine*, fourth series, volume II., subsequently formed the first chapter of *Clausius' Theory of Heat*, 1864, was for the second time converted into English in the translation of that work by Hirst in 1867, and in 1898 it reappeared, with notes by Max Planck as volume 99 of the *Ostwald's Klassiker*. No one questions the interest and importance of this paper, nor of the others which have been gathered together with it to form this volume of the scientific memoirs. It is unquestionably a useful thing to gather three related treatises from different sources together within the same covers. Still less would any critic be inclined to object to anything which might lead to a wider dissemination of such literature; but are there not very many papers as important and as closely related to one another as these, which are inaccessible, and which might with still greater service to the scientific public be grouped together?

The third of the reprints under consideration is not open to the above objections. In culling from *Faraday's Experimental Researches* those sections which deal with electrolysis, and arranging them so as to form a straightforward and consistent treatise, Professor Goodwin has done the scientific public a real service. Faraday's paper on "Electrochemical Decomposition" forms a fitting introduction to the volume, and the translation of Hittorf's papers, which in spite of their great significance are less widely known than they ought to be, forms a fitting appendix to Faraday's work. The volume ends with a translation of Kohlrausch's brief paper on "Conductivity of Electrolytes Dissolved in Water," in relation to the migration of their components.

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